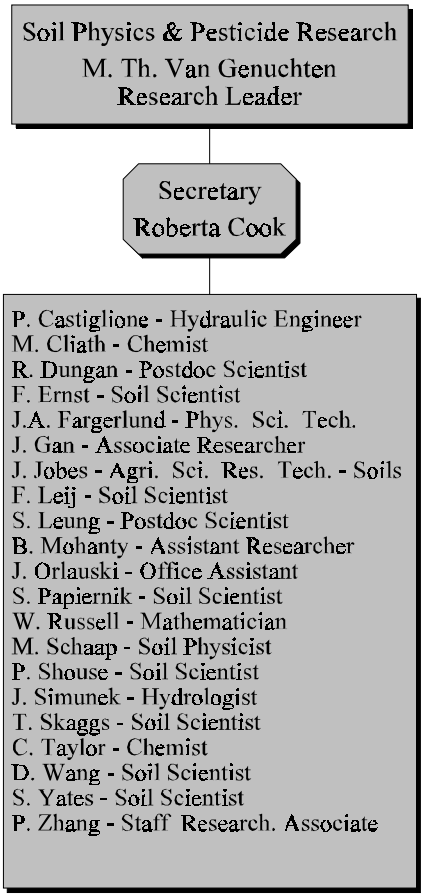
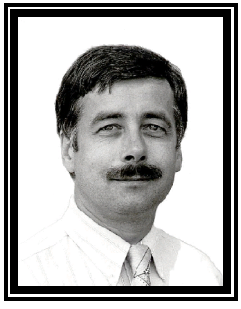
Soil Physics & Pesticide Research



Mission

The mission of the Soil Physics & Pesticide Research unit is to develop methods for evaluating, predicting, and managing the movement of water, salts and agricultural chemicals in the root and vadose zones of salt-affected soils, and to develop tools for assessing new soil-water-crop management schemes to make effective use of limited resources where salinity and/or pesticides area concern. Emphasis is on (1) evaluating the impact of irrigated agriculture on soil and groundwater quality using integrated unsaturated water and solute transport models related user-friendly computer software, (2) pesticide volatilization and pesticide loadings from agricultural fields to surface and ground waters, (3) developing improved methods for measuring unsaturated water and solute transport parameters and related soil properties, (4) characterizing the important physical and chemical processes affecting the fate and transport of harmful pesticides and related organic chemicals into the atmosphere and into the subsurface, and (5) developing methods for evaluating and reducing soil and water contamination by pathogens from the use of animal waste products.

SOIL PHYSICS & PESTICIDE RESEARCH STAFF



MARTINUS Th. van GENUCHTEN, B.S., M.S., Ph.D., Research Leader and Supervisory Soil Scientist of the Soil Physics & Pesticide Research.

Water flow and solute transport in soil and groundwater systems. Analytical and numerical methods for simulating water, heat and/or solute movement in the subsurface. Characterization and measurement of the unsaturated soil hydraulic properties. Use of inverse methods for estimating vadose zone flow and transport parameters. Crop salt tolerance. Root water uptake. Reclamation of salt-affected soils. Preferential flow of water and solutes in aggregated (macroporous) soils and fractured rock. Pesticide transport. Nonequilibrium chemical transport.

SCOTT R. YATES, B.S., M.S., Ph.D. Soil Scientist for Soil Physics & Pesticide Research

Pesticide fate and transport as related to the quality of surface and groundwaters in irrigated areas; test and develop analytical and numerical solutions for the transport of organic compounds in heterogeneous porous media, especially at field scale. Application of models for simulating saturated and unsaturated flow, solute, heat and vapor transport in the subsurface, including the effects of surface volatilization. Other areas of interest include microbial transport, hillside seepage processes, applications of geostatistics and other techniques for describing field-scale spatial variability.

SHARON PAPIERNIK, B.A., Ph.D., Soil Scientist for Soil Physics & Pesticide Research.

Laboratory and field investigations of the environmental fate of pesticides; sorption/desorption, transformation, and transport of fumigants and other pesticides and the interaction of these processes; development of management practices to minimize environmental contamination by pesticides while maintaining efficacy; improved methods of laboratory analysis of pesticides and their properties.

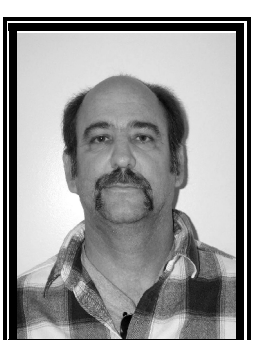
SOIL PHYSICS & PESTICIDE RESEARCH STAFF

DONG WANG, B.S., M.S., Ph.D., E.I.T. Soil Scientist for Soil Physics & Pesticide Research.

Drip, sprinkler, furrow irrigation systems; processes and mechanisms attributing to soil and water salinity; environmental biophysical factors affecting plant growth under saline environment; heat and mass transfer in the soil-water-plant-atmosphere continuum.

TODD SKAGGS, B.S., Ph.D., Soil Scientist for Soil Physics & Pesticide Research.

Field, laboratory, and theoretical investigations of flow and transport processes in soils; fate and transport of salts and agricultural chemicals in groundwater; improved methods for treating spatial and temporal variability.



PETER J. SHOUSE, B.S., Ph.D., Soil Scientist for Soil Physics & Pesticide Research.

Laboratory and field investigations that quantify the fundamental processes of water and salt movement in naturally heterogeneous soils, and the response of plants to water and salinity stress.

MULTI-FLUID HYDRAULIC PROPERTIES FOR FRACTIONAL WETTABILITY POROUS MEDIA

S.A. Bradford, L.M. Abriola and F.J. Leij

The theory for the prediction and modeling of multiphase hydraulic properties has largely relied on the simplifying assumptions that water completely wets the solid surface and, in the case of three-fluid systems, that the organic spreads to form a continuous intermediate wetting phase. More complex fluid distributions may occur in many natural systems due to spatial and temporal variations in fluid and solid properties. In some instances the porous media can have both water- and organic-wet solid surfaces. This condition is referred to as fractional wettability. This paper reviews methods that have been developed by the authors over the past several years to measure, model, and predict hydraulic property relations for fractional wettability soils containing two (organic liquid and water) or three (air, organic liquid, and water) fluids. Fractional wettability systems exhibited saturation dependent wettability effects on the hydraulic property relations. For a given saturation history, increasing the organic-wet fraction tended to decrease the organic relative permeability and the organic-water capillary pressure (organic minus water pressure). The predictive procedures discussed herein were assessed with independent experimental data. Results indicate that these methods, used in conjunction with wettability indices, could provide reasonable predictions of the fractional wettability hydraulic properties. The predictions for three-fluid systems were more speculative due to the formation of a discontinuous intermediate phase, and the lack of relative permeability data for model comparison.

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media*, *Part* 1, pp. 165-178, University of California, Riverside, CA, 1999.

MEASUREMENT OF INITIAL SOIL-WATER CONTACT ANGLE OF WATER REPELLENT SOILS

M.L.K. Carrillo, J. Letey and S.R. Yates

Water repellent soils are common throughout the world. Water repellency significantly affects infiltration, evaporation, and other water-soil interactions. Various indices, such as the water-solid contact angle (θ), water drop penetration time (WDPT), and 90° surface tension (γ_{ND}), have been proposed to characterize the degree of water repellency. The water repellency of many soils is not stable, but changes with time after contact with water. No method is available to measure the initial soil-water contact angle. The purpose of this study was to establish a technique to measure the initial soil-water contact angle. We combined previously published theoretical relationships to develop the equations $\cos\theta=[(\gamma_{ND}/\gamma_w)^{1/2} - 1]$ and $h_p = 2[(\gamma_w\ \gamma_{ND})^{1/2} - \gamma_w]/r\rho g$, where γ_w is the water surface tension, h_p is the breakthrough pressure head, r is the pore radius, ρ is the water density, and g is the gravitational constant. The validity of these relationships was established by treating two sand materials with octadecylamine or solvent extracts from peat moss to create various levels of water repellency. An instrument was developed to measure h_p. *A* linear relationship was found between h_p and $\gamma_{ND}^{1/2}$ as specified by the equation. The value of r was computed from the slope h_p *vs.* $\gamma_{ND}^{1/2}$ curve, and this r value was combined with h_p in the capillary rise equation to compute $\cos\theta$. Good agreement was found between measured and predicted relationships between $\cos\theta$ and $\gamma_{ND}^{1/2}$. The major conclusion is that the value of θ can be determined by measuring γ_{ND}, which is easily done in the field or laboratory.

Soil Sci. Soc. Am. J. 63:433-436, 1999.

UNSTABLE WATER FLOW IN A LAYERED SOIL: I. EFFECTS OF A STABLE WATER-REPELLENT LAYER

M.L.K. Carrillo, J. Letey and S.R. Yates

The development of preferential water flow in a soil profile can cause accelerated movement of pollutants to the groundwater thus reducing groundwater quality. This study investigated the effects of a stable water-repellent soil layer on the development of unstable water flow in a homogenous profile. Stable w~ter-repellent soil is defined as one whose degree of water repellency does not change with time after contact with water. The effects of water entry pressure (h_p), water-repellent layer depth (L) and depth of ponded water at the soil surface (h_0) on the development of unstable flow were investigated using homogenous coarse sand packed into a specially built rectangular chamber. The hydraulic conductivity of the water repellent soil was also measured as a function of h_p and h_0 in a separate experiment using the constant head method. The hydraulic conductivity and the water content of the water repellent soil increased as h_0/h_p increased. No water penetrated the water repellent layer for values of $(h_0 + L)/h_p < 1$, unstable flow developed for values between 1 and 1.5 and a stable front developed for values > 1.5. The conclusion is that stable flow occurred when the water flux through the water repellent layer exceeded the saturated hydraulic conductivity of the underlying wettable layer. The water flux through the water repellent layer was a function of the hydraulic conductivity of the water repellent layer which increased as h_0/h_p increased.

Soil Sci. Soc. Am. J. 64:450-455, 2000.

UNSTABLE WATER FLOW IN A LAYERED SOIL: II. EFFECTS OF AN UNSTABLE WATER-REPELLENT LAYER

M.L.K. Carrillo, J. Letey and S.R. Yates

Water repellent soils are found throughout the world and can exhibit significantly different water flow characteristics as compared to a wettable soil. The purpose of the study was to determine the significance of the stability of the water repellency on the development of unstable water flow below a water repellent layer. Unstable water-repellent soil refers to a soil whose degree of repellency changes with time after contact with water. Experiments were conducted in a specially built rectangular chamber where wetting front patterns could be observed through a Plexiglas sheet. The experiments were done on water repellent sand layers that were treated to create water drop penetration time (WDPT) values of 1, 10, and 150 min. The WDPT of the layer and the ratio $(h_0 + L)/h_p$ were important in the development of ringers, where h_0 is the depth of ponded water at the soil surface, L is the depth of the water repellent layer and h_p is the water entry pressure head of the water repellent layer. For low WDPT (1 min) no fingers formed. As the WDPT increased, the tendency for finger formation also increased. The medium WDPT (10 min) layer caused finger formation, however, the fingers broadened and converged after continued flow and an almost uniform wetting front eventually developed. The combination of a high WDPT (150 min) and $(h_0 + L)/h_p$ <1 produced the most dramatic and persistent fingering. The finger development across the layer and the flux through the layer was found to be a function of time. Water repellency at the soil surface has the greatest impact on infiltration because water depth may not be sufficient to overcome the water entry pressure and runoff would decrease the time of exposure to water to overcome unstable water repellency.

Soil Sci. Soc. Am. J. 64:456-459, 2000.

MEASUREMENT OF SOLUTE RESIDENCE CONCENTRATION IN VARIABLY-SATURATED SOILS BY TIME DOMAIN REFLECTOMETRY: A NEW CALIBRATION PROCEDURE

P. Castiglione, B.P. Mohanty, P.J. Shouse and M. Th. van Genuchten

Traditionally the TDR technique for measuring solute residence concentration is based on measurement of the d.c. electrical conductivity of bulk soil, which is strongly dependent on the water content and its solute concentration. A pulse voltage propagating through the transmission line, made up of the TDR probe - soil system, is subject to dispersion and attenuation, depending on the dielectric permettivity and electrical conductivity of the soil. Since no exact model for the wave propagation in TDR-soil systems is available, the above characteristics are usually deducted from the analysis of the reflected signal in the time domain, through calibration procedures.

The simplified lumped-circuit model of Giese Tiernann is commonly employed to relate the d. c. conductivity of the soil to the attenuation of the reflected signal at large time, which correspond to low frequencies as stated by the Fourier theory. We carried out a series of measurements in electrolytic solutions for different probe and coaxial cable lengths. Our results showed that this kind of analysis is inadequate if the losses along the cable are not adequately taken into account. A discussion of a distributed-circuit model proposed by Dalton and van Genuchten (1986) is also reported.
The relationship among bulk soil electrical conductivity, water content and solute residence concentration is a characteristic of the soil, and depends on its pore size distribution. Therefore, it can only be determined by a calibration procedure. Usually this consists of TDR measurement of the electrical conductivity in several samples at equilibrium. The water content and solute resident concentration of the samples are then independently measured.

We propose a new calibration procedure, which is based on a series of drainage-leaching cycles on a single soil column. Our procedure utilizes the advantage of measuring the electrical conductivity and the water content over the same sample volume by using the TDR technique. Our experimental results show that within a range of water contents, whose range depends on the soil type, it is possible, by means of the dimensional analysis, to determine a unique relationship among the above mentioned quantities. This procedure, moreover, allows one to easily take into account the electrical conductivity of the solid matrix of the soil, which is often non-negligible.

Am. Geophys. Union, p. 502, 2000.

QUANTIFICATION OF SOIL MACROPORE/MATRIX PROPERTIES USING CONTRIVED COLUMN EXPERIMENTS

P. Castiglione, B.P. Mohanty, P.J. Shouse and M. Th. van Genuchten

Preferential flow is recognized to occur in many agricultural soils. This process is defined as the rapid movement of water and solutes via larger pores bypassing the micropores. Multi-domain models account for the non-equilibrium phenomena characterizing flow/transport in such a condition. Yet, inability to determine the hydraulic/transport properties of each domain separately, severely limits their use. The main goal of this research is to study hydraulic characteristics of the matrix and macropore domains and to investigate the conditions needed for the preferential flow to be activated. A repacked soil column with artificial macropores was designed and created. In this paper, results of transient and steady state infiltration experiments with a non-reactive tracer are presented. The influence of pore geometry as well as the initial and boundary conditions on the macroscopic features of the flow-transport phenomena is discussed.

Agronomy Abstract p. 194, 1999.

FLOW AND TRANSPORT THROUGH A BIPOROUS MEDIUM: EXPERIMENTAL FINDINGS AND NUMERICAL MODELING

P. Castiglione, B.P. Mohanty, P.J. Shouse and M. Th. van Genuchten

Prior research findings show that flow and transport through macroporous medium need to be characterized by nonequilibrium. processes between high and low permeability domains. Such phenomena are usually modeled at the Darcy scale by adopting a multi-domain model based on up-scaling of microscopic heterogeneity to macroscopic processes. In this paper we present flow and transport experimental results from a soil column containing artificial macropores of known geometry. Multiple TDRs located at different depths of the column allowed the monitoring of water and solute breakthrough curves (BTCs) at these depths. Different forward and inverse models were used to analyze BTC data at single or multiple depths. Our analysis revealed inadequacy of such methods using a single BTC. We also showed limitations of the widely adopted Mobile-Immobile model when the soil matrix conductivity is significant with respect to macropore conductivity. Our findings suggest that the macroscopic features of the preferential flow process are strongly dependent on the observation scale. Based on our controlled experimental data we proposed a new physically based procedure for the estimation of transport parameters of a dual-permeability model.

Agronomy Abstract p. 217, 2000.

ON-LINE SYSTEM FOR VOLATILIZATION MEASUREMENT OF VOCS FROM SOIL

F.F. Ernst, J. Gan, C. Taylor, Q. Zhang, S.K. Papiernik and S.R. Yates

Volatilization of organic compounds is traditionally measured by first trapping the organic vapors on an adsorbent and then quantifying the concentration following sample preparation. This approach is expensive, labor intensive and time consuming, which generally prohibits extensive sample collection. We developed an on-line sampling system that performs real-time sample collection and analysis. Vapors leaving the soil surface are directly swept into a GC, while the use of computer-controlled multiple channels and solenoid valves allows automatic and sequential measurement from multiple volatilization sources. No adsorbent or solvent is needed, and manual input is minimal. This technique was used for continuously measuring emission of three soil fumigants from four soil columns for 11 days, and was found to generate extremely detailed and descriptive volatilization dynamics for each fumigant from each column.

Agronomy Abstract p. 184, 1999.

APPLICATION OF AMMONIUM THIOSULFATE TO REDUCE TELONE II EMISSIONS FROM SOIL

J. Gan, S.K. Papiernik, J.0. Becker, J.A. Knuteson and S.R. Yates

The anticipated phase-out of methyl bromide (MeBr) has stimulated an intensive search for effective alternatives. 1,3-Dichloropropene (Telone II, or 1,3-D), used alone or in combination with chloropicrin, is considered as one of the most promising MeBr replacements. However, both isomers of 1,3-D are highly volatile. A number of studies have shown that 11-90% of applied 1,3 -D can escape into the air after soil fumigation. Because 1,3-D is acutely toxic and potentially carcinogenic, excessive emissions of its vapor into the atmosphere may contribute to air pollution and cause detrimental effects to human health and the environment. Thus, in order to continue Telone fumigation in an environment-compatible manner, it is important to develop mitigation practices to reduce its emissions while sustaining its effectiveness for pest control.

Atmospheric emissions of a fumigant can be reduced if the fumigant's volatility is eliminated because of degradation or transformation of the parent compound. In our recent work we have identified thiosulfate products as highly efficient reactants for MeBr, 1,3-D, chloropicrin, methyl iodide, and propargyl bromide. Thus, thiosulfate products may be used as surface reactants to suppress emissions of these fumigants. As ammonium and potassium thiosulfates are commercial fertilizers, this mitigation approach is cost-effective and simple to implement. Here we report transformation of 1,3-D by ammonium thiosulfate (ATS) in soil under different conditions, and experiments demonstrating reduction in Telone II emissions after surface amendment of ATS.

Transformation of 1,3-D in ATS-amended soil was proportional to the relative ratio of ATS to l,3-D. As shown in Table 1, the half-life of 1,3-D in soil was reduced from 256 h (-10 d) in the non-amended soil to 18 h when the ratio was 2: 1, and further to only 4 h when the ratio was 4: 1. Similar relationships between ATS amendment levels and 1,3-D transformation were observed for both Arlington and Carsitas soils, indicating that ATS-induced 1,3-D transformation was independent of soil type (Table 1). Overall, as the ratio of ATS to 1,3 -D was doubled, the half-life of 1,3-D was halved.

We subsequently conducted column experiments to evaluate the reduction of 1,3-D emissions by surface amendment of ATS. In large columns packed with Arlington sandy loam, 1,3-D emission rate (% of applied dosage) decreased rapidly with increasing ATS application rate (Figure I). When ATS was applied in 9 mm water at 64 g m^{-2}, total 1,3-D emission was reduced by 61%. The reduction increased further to 89% when ATS was applied at 193 g m^{-2}.

Proceedings of the 1999 Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reductions. Nov. 1-4, 1999, San Diego, CA. 94:1-3, 1999.

EVALUATION OF ACCELERATED SOLVENT EXTRACTION (ASE) FOR ANALYSIS OF PESTICIDE RESIDUES IN SOIL

J. Gan, S.K. Papiernik, W.C. Koskinen and S.R. Yates

Accelerated solvent extraction, or ASE, is a new extraction technique that is similar in principle to Soxhlet extraction, but the use of elevated temperature and pressure with ASE allows the extraction to be completed within a short time and with a small quantity of solvent. In this study, we investigated the effect of residue aging, solvent type, and ASE conditions on the recovery of atrazine and alachlor from different soils, and compared the efficiency of ASE with that of Soxhlet and solvent-shake extractions. With ASE, the use of dichloromethane-acetone (1: 1, v/v) or methanol as solvent resulted in significantly greater pesticide recovery than hexane. After the residue was aged for >2 weeks, pesticide recovery was significantly influenced by the extraction temperature in ASE vessel, and the recovery increased to 130-140°C and then decreased. The efficiency of ASE was generally better than that for Soxhlet or shake extraction using methanol-water (4: 1, v/v). ASE extraction also consumed considerably less solvent than the other two conventional methods.

Environ. Sci. Technol. 33:3249-3253, 1999.

TEMPERATURE AND MOISTURE EFFECTS ON FUMIGANT DEGRADATION IN SOIL

J. Gan, S.K. Papiernik, S.R. Yates and W.A. Jury

Recent discovery of the contribution of methyl bromide fumigation to stratospheric ozone depletion has revealed our limited understanding of the environmental processes of fumigants. For instance, little is known about fumigant degradation in soil under high temperature or low moisture conditions that prevail near the soil surface during fumigation. In this study we determined the interaction of soil temperature and moisture with degradation of 1,3-dichloropropene (1,3-D) and methyl isothiocyanate (MITC) for extended soil temperature and moisture ranges. Fumigant degradation increased 5 to 12 times when temperature increased from 20 to 50°C. It was further shown that chemical transformation of fumigants always increased with increasing temperature, but temperature effects on microbial degradation were fumigant dependent. The relative contribution of microbial degradation to the overall fumigant degradation was highest for the soil with highest organic matter content, and was greater for MITC than for 1,3-D isomers. When the temperature was >30°C, microbial degradation of 1,3-D was substantially suppressed, while that of MITC was greatly stimulated. As soil moisture content increased, 1,3-D degradation accelerated, but that of MITC decreased. The specific responses of fumigant degradation to temperature and moisture variations should be considered when describing their transport in the environment, and also may be used for designing fumigation practices that allow reduced atmospheric emissions.

J. Environ. Qual. 28:1436-1441, 1999.

ENHANCED FUMIGANT ACITVITY AT HIGHER SOIL TEMPERATURE

S.K. Xue, J. Gan, J.O. Becker, S.R. Yates and S.K. Papiernik

In soil solarization, temperature increases are typically the greatest near the soil surface, and gradually diminish with depth. Consequently, soil solarization provides good pest control near the surface, and often inadequate suppression for deep layers. Soil solarization combined with fumigation at regular or reduced rates was found to substantially improve pest control compared to solarization or fumigation alone. The enhanced efficacy was caused by synergistic interactions between fumigants and temperature. Synergistic interactions between fumigants and temperature are potentially useful in that they may be used for designing integrated practices to improve the efficacy of solarization. In particular, if the synergism allows lower rates of fumigants to be used, environmental input of chemical fumigants will also be reduced. So far, however, fumigant-temperature interactions have not been systematically studied. The main objective of this study was to determine the interaction between soil temperature and activities of methyl bromide (MeBr) and 1,3-dichloropropene (1,3-D) against citrus nematode ***Tylenchulus semipenetrans.***

Soil (50 g) in 170 mL glass bottles was inoculated with about 600 nematode juveniles extracted from infested citrus roots, and then exposed to MeBr and 1,3-D at 20, 30, 40, and 45°C. After exposure for 6,12,24,48, and 96 h, replicate samples (x 4) were extracted on Baermann funnels and the remaining nematode density was enumerated. Two replicate samples were simultaneously removed for analysis of residual fumigant concentrations. Concentration-time index (ct) was calculated, and correlated with nematode mortality. Soil samples not treated with fumigants also received the same temperature treatments.

In untreated soil, nematode survival was not significantly affected by temperature in the range of 20-30°C, but was strongly reduced at temperature $\geq$40°C. This suggests that temperatures $\geq$40°C were lethal for *Tylenchulus semipenetrans***,** while a temperature $\leq$30°C was sublethal. In fumigated soil, nematode suppression was a combined result of fumigant activity and temperature effect. For the same fumigant rate, nematode suppression was closely dependent on the temperature of incubation. Nematode suppression at 40°C in fumigated soils was similar to that in untreated soil, indicating that temperature alone was sufficient to provide the activity. Nematode responses to temperature were different between 20°C and 30°C. In general, much less time was required for the same rate to achieve 100% nematode suppression at 30°C than at 20°C. Likewise, at all levels, after exposure for the same time, greater suppression of nematodes occurred at 30°C than at 20°C. In contrast, in untreated soil, nematode survival was found.to be unaffected at 20 and 30°C. This implies that synergistic reaction occurred between temperature and fumigant, which resulted in a higher fumigant activity at 30°C than at 20°C.

Proc. of the Annual Int. Res. Conf. On Methyl Bromide Alternatives and Emissions Reductions. Nov. 1-4, San Diego, CA. 95:1-3, 1999.

CONCENTRATION- AND TEMPERATURE- DEPENDENT DEGRADATION OF TWO FUMIGANTS IN A SANDY SOIL

Q.L. Ma, J. Gan, S.K. Papiernik, J.O. Becker and S.R. Yates

Soil temperature and fumigant concentration on degradation of methyl isothiocyanate (MITC) and 1,3-dichloropropene (1,3-D) in Arlington sandy loam (coarse loam, mixed, thermic, hapllic Duroxeralf) were studied and an inverse first-order model was proposed to describe the concentration-degradation rate relationship. At the same concentration, degradation of MITC and 1,3-D increased with temperature from 20 to 40 C and followed the Arrhenius equation ($r^2 > 0.81$). At the same temperature, degradation rates of both fumigants were inversely proportional to concentration and were well described by an inverse first-order equation ($r^2 > 0.89$). Degradation rates of MITC varied by approximately an order of magnitude in the concentration range of ~3 and 140 mg kg^{-1}, depending on temperature. Likewise, degradation rates of (E)1,3-D isomer varied between 2.1 and 4.1 times, and of (Z)- 1,3-D isomer between 1.5 and 2.9 times, in the concentration range of 0.6 and 60 mg kg^{-1}. It is suggested that pesticide fate models should include both temperature and concentration in simulating dissipation of MITC and 1,3-D in the field.

Agronomy Abstract p. 312, 2000.

REDUCE PESTICIDE AIR POLLUTION WITH REACTIVE FERTILIZERS

J. Gan and S.R. Yates

Soil fumigants are a class of highly volatile pesticides. They are used in warm regions for treating soils to eradicate soilborne pathogens, nematodes and weeds. Most existing fumigants are halogenated Cl-C3 compounds, including methyl bromide (MB), 1,3-dichloropropene (1,3-D), and chloropicrin (CP). Two more halogenated hydrocarbons, methyl iodide (MI) and propargyll bromide (PB), are currently being investigated as alternatives to MB. These halogenated fumigants share similar properties such as high volatilization potential, high acute toxicity, and potential mutagenicity. These characteristics together suggest that atmospheric emissions of these products may become a significant source of air pollution that can inflict hazardous effects on field workers or nearby residents. Therefore, feasible measures to suppress fumigant emissions are imperatively needed.

We have discovered that these halogenated fumigants can all undergo nucleophilic substitution reaction With thiosulfate salts such as ammonium-, sodium-, potassium-, and calcium thiosulfate. Transformation by thiosulfate greatly decreased the activity of these fumigants, and also converted them into non-volatile dehalogenated anions. We have carried out systematic experiments to develop protocols to use thiosulfate salts for reducing fumigant volatilization from soil. Because many thiosulfate salts are commercial fertilizers and thus available at a low cost, the use of thiosulfate fertilizers to reduce fumigant emissions represents one of the most feasible option. So far we have completed several column experiments and field trials to evaluate reductions of emission achieved by surface amendment of ammonium thiosulfate (ATS), and factors affecting the magnitude of reduction. We report such applications using 1,3-D as an example.

ACS 219th National Meetings in San Francisco, CA, 40(1), 2000.

COLUMN SYSTEM FOR CONCURRENT ASSESSMENT OF EMISSION POTENTIAL AND PEST CONTROL OF SOIL FUMIGANTS

J. Gan, C. Hutchinson, F.F. Ernst, J.0. Becker and S.R. Yates

Fumigation for soilborne pest and pathogen control is under close scrutiny because of its potential hazardous effects on the environment and on human health. Therefore, reduced-risk yet effective fumigation practices are imperatively needed. We have developed a column system that allows an integrated evaluation of emission potential and efficacy of fumigants. The system consists of a large, packed soil column and a sampling chamber for measuring fumigant emissions at the soil surface. Nematodes (or other pests) can be inoculated into the column and their survival may be assayed after the treatment. This approach was used to evaluate the emission of 1,3-dichloropropene (1,3-D) and its efficacy against the citrus nematode *Tylenchulus semipenetrans* when ammonium thiosulfate, a 1,3-D degrading fertilizer, was applied at the soil surface. Results closely comparable to field observations were obtained. Compared with field studies, the proposed method is rapid and inexpensive, and thus may be used for screening fumigation practices that have improved environmental safety and pest control performance.

J. Environ. Qual. 29:657-661, 2000.

DEGRADATION AND VOLATILIZATION OF THE FUMIGANT CHLOROPICRIN AFTER SOIL TREATMENT

J. Gan, S.R. Yates, F.F. Ernst and W.A. Jury

Chloropicrin (CP) is used in fumigation of soil-borne pests. Because of its high volatility and toxicity, atmospheric emission of CP during soil application may become a source of air pollution. We investigated degradation of CP in three different soils as a function of soil temperature and moisture conditions, and evaluated its volatilization against methyl bromide (MeBr) from packed soil columns. Chloropicrin degraded much faster than MeBr in the same soil, mainly via microbial degradation. Degradation of CP accelerated as soil temperature increased, but was relatively independent of changes in soil moisture. When the soil surface was uncovered, overall volatilization loss of CP was similar to that of MeBr. Covering the soil surface with a polyethylene or high-barrier film was much more effective in reducing volatilization of CP than MeBr. Therefore, surface covers may be used in sensitive areas to reduce human exposure to CP.

J. Environ. Qual. 29:1391-1397, 2000.

TEMPERATURE AND MOISTURE EFFECTS ON FUMIGANT DEGRADATION IN SOIL

J. Gan, S.K. Papiernik, S.R. Yates and W.A. Jury

Recent discovery of the contribution of methyl bromide fumigation to stratospheric ozone depletion has revealed our limited understanding of the environmental processes of fumigants. For instance, little is known about fumigant degradation in soil under high temperature or low moisture conditions that prevail near the soil surface during fumigation. In this study we determined the interaction of soil temperature and moisture with degradation of 1,3-dichloropropene (1,3-D) and methyl isothiocyanate (MITC) for extended soil temperature and moisture ranges. Fumigant degradation increased 5 to 12 times when temperature increased from 20 to 50°C. It was further shown that chemical transformation of fumigants always increased with increasing temperature, but temperature effects on microbial degradation were fumigant dependent. The relative contribution of microbial degradation to the overall fumigant degradation was highest for the soil with highest organic matter content, and was greater for MITC than for 1,3-D isomers. When the temperature was >30°C, microbial degradation of 1,3-D was substantially suppressed, while that of MITC was greatly stimulated. As soil moisture content increased, 1,3-D degradation accelerated, but that of MITC decreased. The specific responses of fumigant degradation to temperature and moisture variations should be considered when describing their transport in the environment, and also may be used for designing fumigation practices that allow reduced atmospheric emissions.

J. Environ. Qual. 28:1436-1441, 1999.

SURFACE APPLICATION OF AMMONIUM THIOSULFATE TO REDUCE 1,3-DICHLOROPROPENE VOLATILIZATION FROM SOIL

J. Gan, J.O. Becker, F.F. Ernst, C. Hutchinson, J.A. Knuteson and S.R. Yates

Atmospheric emission of the soil fumigant 1,3-dichloropropene (1,3-D) is of environmental concern because of its toxicity and carcinogenicity. Thiosulfate fertilizers were previously found to rapidly transform 1,3-D to non-volatile, less toxic ions in soil. In this study, we investigated the use of surface application of ammonium thiosulfate (ATS) for reducing 1,3-D volatilization. In packed soil columns, 1,3-D emission decreased with increasing ATS application rate and the amount of water used for delivering ATS. When ATS was applied in 9 mm water at 64 g m^{-2}, total 1,3-D emission was reduced by 61%. The reduction increased further to 89% when ATS was applied at 193 g m^{-2}. Bioassays showed that ATS application did not affect 1,3-D's effectiveness for controlling inoculated citrus nematodes. In field plots where 1,3-D was applied via subsurface drip, surface spray of ATS reduced 1,3-D emissions by 50% when the soil surface was not tarped, and by 71% when the surface was tarped with polyethylene sheets. ATS application had no effect on the efficacy of root-knot nematode control or tomato yields. These results suggest that surface application of thiosulfate fertilizers is a feasible and effective strategy for minimizing 1,3-D emissions, and should be further explored.

Pest. Management Science 56:264-270, 2000.

TRANSFORMATION OF 1,3-DICHLOROPROPENE IN SOIL BY THIOSULFATE FERTILIZERS

J. Gan, S.R. Yates, J.A. Knuteson and J.O. Becker

The pesticide 1,3-dichloropropene (1,3-D) is considered to be the most promising alternative to methyl bromide for soilborne pest control. The high volatility of 1,3-D, however, has been shown to result in excessive atmospheric emissions that may impose toxicological effects on workers or residents. This study demonstrated that 1,3-D was rapidly transformed to nonvolatile products by thiosulfate fertilizers in soil, and that thiosulfate-facilitated fumigant transformation may be used to reduce 1,3-D emissions. Transformation of 1,3-D by thiosulfate was chemically based, and 1,3-D degradation in soil accelerated proportionally as thiosulfate level in soil increased. At a 4:1 thiosulfate to fumigant molar ratio, the half-life of 1,3-D was reduced to only a few hours, as compared with > 10 d for nonamended soils. The rate of thiosulfate-facilitated 1,3-D transformation was independent of soil types and was higher in moist soils and at high soil temperatures. Transformation occurred at a similar rate for ammonium, calcium, and sodium thiosulfates. As these thiosulfate compounds are commercial fertilizers, amendment of these products at the soil surface during 1,3-D fumigation may offer an effective and inexpensive approach for reducing 1,3.D emissions.

J. Environ. Qual. 29:1476-1481, 2000.

NEMATODE RESPONSE TO METHYL BROMIDE AND 1,3-DICHLOROPROPENE SOIL FUMIGATION AT DIFFERENT TEMPERATURES

S.K. Xue, J. Gan, S.R. Yates and J.O. Becker

Several heat-based methods, such as soil solarization, are being developed as alternative practices for managing soilborne pests and pathogens. The effectiveness of these practices is often inconsistent or marginal, thus commanding the need for their integration with other methods. The main objective of this study was to determine synergistic interaction between soil fumigants and temperature. Citrus nematode *Tylenchulus semipenetrans* infested soil was exposed to methyl bromide (MeBr) or 1,3-dichloropropene (1,3-D) at various temperatures. Fumigant degradation was concurrently measured and concentration-time index (ct) were calculated and correlated to the recovered nematode population. In untreated soil, nematode survival was not affected from 20 to 30°C, but was strongly reduced at ≥ 40°C. In fumigated soil, nematode suppression was much greater at 30°C than at 20°C, and the ct required for nematode elimination at 30°C was only <50% of that needed at 20°C for both fumigants. These results suggest that these fumigants became more active with increasing temperature in the sub-lethal temperature range. It also implies that when integrated with a heat-based practice, reduced rates of fumigants may provide adequate pest control, thus minimizing the environmental input of chemical fumigants.

Pest Management Science 56:737-742, 2000.

ADSORPTION AND CATALYTIC HYDROLYSIS OF DIETHATYL-ETHYL ON HOMOIONIC CLAYS

W.P. Liu, J.

Gan, S.K. Papiernik and S.R. Yates

Adsorption and catalytic hydrolysis of the herbicide diethatyl-ethyl [N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester] on homoionic Na^+, K^+-, Ca^{2+}-, and Mg^{2+}- montmorillonite clays were studied in aqueous media. The Freundlich adsorption coefficient, Kf, measured from isotherms on clay followed the order of $Na^+ \approx K^+ > Mg^{2+} \approx Ca^{2+}$. Analysis of FT-IR spectra of diethatyl-ethyl adsorbed on clay suggests probable bonding at the carboxyl and amide carbonyl groups of the herbicide. The rate of herbicide hydrolysis in homoionic clay suspensions followed the same order as that for adsorption, indicating that adsorption may have preceded and thus caused hydrolysis. Preliminary product identification showed that hydrolysis occurred via nucleophilic substitution at the carboxyl carbon, causing the cleavage of the ester bond and formation of diethatyl and its dechlorinated derivative, and at the amide carbon, yielding an ethyl ester derivative and its acid. These pathways also suggest that hydrolysis of diethatyl-ethyl was catalyzed by adsorption on the clay surface.

J. Agric. Food Chem. 48:1935-1940, 2000.

STRUCTURAL INFLUENCES IN RELATIVE SORPTIVITY OF CHLOROACETANILIDE HERBICIDES ON SOIL

W. Liu, J. Gan, S.K. Papiernik and S.R. Yates

Adsorption of the chloroacetanilide herbicides acetochlor, alachlor, metolachlor and propadhlor was determined on soils and soil components, and their structural differences were used to explain their sorptivity orders. On all soils and soil humic acids, adsorption decreased in the order: metolachlor > acetochlor > propachlor > alachlor. On Ca^{2+}-saturated montmorillonite, the order changed to metolachlor > acetochlor > alachlor > propachlor. FT-IR differential spectra of herbicide-clay or herbicide-hurnic acid-clay showed possible formation of hydrogen bonds and charge transfer bonds between herbicides and adsorbents.. The different substitutions and their spatial arrangement in the herbicide molecule were found to affect the relative sorptivity of these herbicides by influencing the reactivity of functional groups participating in these bond interactions. It was further suggested that structural differences of pesticides from the same class may be used as a molecular probe to obtain a better understanding of adsorption mechanisms of pesticides on soil.

J. Agric. Food Chem. 48:4320-4325, 2000.

EFFECTS OF COMPONENT INTERACTIONS ON HERBICIDE ADSORPTION

J. Gan, W.P. Liu, S.K. Papiernik and S.R. Yates

Pesticide adsorption on soil is known to depend closely on organic matter (OM) and clay compositions. Adsorption in OM-clay mixtures, however is often significantly less than the sum of adsorption on the individual components, suggesting component interaction results in modified adsorption behavior. We determined adsorption of a few acetanilide herbicides in mixtures of humic acid (HA) and montmorillonite. As the ratio of HA to clay increased, Kd first decreased and then increased, but was always smaller than what might be estimated by assuming independent adsorption. A mathematical relationship was developed to describe this phenomenon. The deviation from independent adsorption varied also with the type of herbicide and the interacting time between the adsorbing components. It is likely that the interaction changed the available adsorption sites, and thus the overall adsorption.

Agronomy Abstract p. 336, 1999.

ASSESSMENT AND EMISSION REDUCTION OF METHYL BROMIDE ALTERNATIVE FUMIGANTS

J. Gan, S.R. Yates, J.O. Becker and W.A. Jury

The imminent phase-out of methyl bromide (MeBr) has stimulated an intensive search for alternatives. Chemical alternatives to MeBr include 1,3dichloropropene, methyl isothiocyanate, chloropicrin, methyl iodide, and propargyl bromide. These compounds are all highly volatile and toxic, and some are carcinogenic. Their emissions into the air during use may impose great risks to workers and residents. This project aims to evaluate emission potential of these fumigants under typical application practices, to understand factors that influence their volatilization, and to develop feasible measures to reduce their emissions. We have so far obtained a systematic understanding of fumigant behavior such as transformation and transport, and identified variables that control emission. This information will be used for assessing the relative environmental hazard of different fumigants, and for designing safer fumigation practices.

Agronomy Abstract p. 365, 1999.

PESTICIDES PARTITIONING IN A CREEPING BENTGRASS PUTTING GREEN

L. Wu. R. Green, M.V. Yates, J. Gan, S.R. Yates and G. Liu

Turfgrass is one the most intensively managed biotic systems in the urban landscape. The purpose of this study was to determine the fate of four pesticides (chlorothalonil, metalaxy, chlopyrifos, and trichlorfon) when applied to turfgrass in an environment that closely resembles golf-course conditions. Partitioning of the four pesticides in a creeping bentgrass (Agrostis palustris Huds.) putting green was monitored for volatilization loss, clipping removal, leaching below the root-zone, and distribution in the soil profile. Results showed that volatilization mainly occurred at the initial period after pesticide application. The total amount of volatilization was in the range of 0.01 to 2.8% of the applied pesticides. Clipping removal was very small, ranging from 0.03 to 0.21 %. Under normal management practices, pesticide leaching was minimal. The cumulative leaching was less than 0.003% of the applied pesticides. Most of the applied pesticides remained in the surface 2 cm of the profile, where they subjected to rapid degradation.

Agronomy Abstract p. 52, 2000.

INHIBITION OF ADSORPTION ON PESTICIDE REMEDIATION IN SOIL

J. Gan, Q. Wang, S.K. Papiernik and S.R. Yates

Benign chemical transformations can be used to remove organic contaminants from soil. The effectiveness of using such transformations for soil remediation, however, is affected by the adsorption of the contaminant to soil, as adsorption renders the target contaminant inaccessible for the reaction. We studied the influence of soil type and K_d on the transformation rate of a number of pesticides by thiosulfate salts. For non-adsorbing pesticides such as halogenated fumigants, transformation rate was not greatly affected by soil type and the reaction proceeded almost as rapidly as in the aqueous phase. For adsorbing species such as chloroacetanilide herbicides, transformation rate was negatively correlated with the K_d value and was especially slow in organic matter-rich soils. This dependence suggests that the effectiveness of soil remediation using chemical reactions would be soil- and contaminant-dependent, and may not be directly extrapolated from the reaction rate in the aqueous phase.

Agronomy Abstract p. 388, 2000.

DOSE-RESPONSE RELATIONSHIPS BETWEEN METHYL ISOTHIOCYANATE AND BARNYARD GRASS SEEDS IN A SOIL AT DIFFERENT TEMPERATURES

Q.L. Ma, J. Gan, J.O. Becker, S.K. Papiernik and S.R. Yates

Temperature and fumigation rates on germination of barnyard grass seeds (Echinochloa crus-galli) were studied to evaluate the effectiveness of weed management at a reduced fumigation rate and elevated temperature. Fresh soil mixed with the weed seeds was treated with methyl isothiocynate (MITC) at a range of concentrations and then incubated at 20, 30, and 40°C. Samples were taken periodically to determine MITC concentration and weed germination rate. With no fumigation weed germination rate was not significantly affected by temperature between 20 and 40°C. When combined with fumigation, germination rate was significantly reduced. At 7% of the recommended application rate, the time required to inhibit 50% of the germination rate (T_{50}) was 68.4, 17.9 and 8.7 h at 20, 30 and 40°C, respectively. At the same temperature, T_{50} value decreased significantly with increasing fumigation rate. However, the product of dose C and exposure time (T) for 50% of inhibition in germination rate (CT50) was not a constant. A large C resulted in a small CT50 value, and vise versa. The results provide scientific bases for applying impermeable plastic films on soil surface as the films increase the soil temperature and also keep a higher fumigant concentration.

Agronomy Abstract p. 319, 2000.

IMPACTS OF METHYL BROMIDE AND ITS ALTERNATIVES ON SOIL MICROBIAL COMMUNITIES

A.M. Ibekwe, S.K. Papiernik, J. Gan, S.R. Yates, D. Crowley and C.H. Yang

Soil fumigation is the primary method used in reducing soilborne plant pathogens and parasitic nematodes that cause severe damages to high value crops in the warm region of the U.S. It is often required to reduce root-knot nematode populations. The fumigants methyl bromide (MeBr), 1,3-dichloropropene (1,3-D), methyl isothiocyanate (NHTC), and chloropicrin are known to have broad biocidal activity, and their effects on soil bacteria are largely unknown. Recently, the effect of MITC (the toxic degradation product of metam sodium) on soil bacterial population structure and function was studied by the use of traditional heterotrophic activity measures, and biochemical assays. The long-term goal of the research in our laboratory in response to the EPA action is to evaluate new or existing alternative fumigants for control of soilborne plant pathogens to replace methyl bromide in high value crop areas. Biologically-based and environmentally-safe alternatives, such as compost amendment and biosolid application, are being investigated for possible use in integrated management strategies for accelerated degradation of fumigants. The hypothesis governing this practice is that organic amendments, when applied to soil, add different substrates that can be used by soil bacteria for growth. However, soils are fumigated by direct injection into the subsurface soil with little or no surface litter. The impacts of this practice on soil microorganisms have rarely been shown. The impact of fumigants on soil microorganisms is being evaluated in view of their role in sustaining the global cycling of matter and their function in supporting soil quality for productive agriculture. In this paper, we describe the effect of MeBr, NHTC, 1,3-D and chloropicrin on soil microbial population in a laboratory microcosm experiment. Our objectives were to monitor the biocidal effects of these fumigants and compare their ecological effects on soil microorganisms in response to fumigation at recommended application rates. To overcome the drawbacks of studying the effect on individual bacterial strains, since only about 1% of total bacteria in the soil can be cultured, we used the nucleic acid approach by employing different PCR methods to analyze the total bacterial population in our samples. We also used biochemical and metabolic approaches to evaluate how microorganisms respond to certain carbon substrates after fumigation. We used the Biolog system in this study to monitor functional changes by heterotrophs and PLFA/DNA fingerprinting to quantify microbial biomass and community diversity composition. Since microbial biomass as determined by PLFA is based on the relationship between the phylogerry of microorganisms and their PLFA profiles, we believe that the use of PLFA techniques provides an unbiased description of the effects of fumigants on microbial population. This allowed us to interpret the effect of fumigants on different groups of bacteria fungi, and actinomycetes. The total bacterial DNA fingerprinting by denaturing gradient gel electrophoresis (DGGE) provided a complete picture on the effects of these compounds on the dominant bacterial populations. Through this we calculated the structural diversity of the microbial community. This provided distinct diversity value for each sample and we were able to observe changes in bacteria composition over the 12 week study period.

Proceedings of the *1999 Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reductions.* November *1-4,* San Diego, CA. 96:1-3, 1999.

IMPACTS OF FUMIGANT TREATMENT ON SOIL MICROBIAL COMMUNITIES BY DGGE

A.M. Ibekwe, S.K. Papiernik, J. Gan, S.R. Yates, D. Crowley and C.H. Yang

The ability of soil microbial communities to rebound after shock treatment from fumigants is critical to the sustainability of agricultural ecosystems. Culture- independent approaches, namely, PLFA and DGGE were used to determine changes in soil microbial community structure in a microcosm, experiment following application of MeBr, MITC, 1,3-D and chloropicrin. Similarity among the different 16S rDNA profiles from fumigated soil was quantified by analyzing the DGGE band patterns. The Shannon index of diversity H was calculated for each fumigated soil sample. High diversity index was maintained between the control soil and the different fumigants, except Methyl bromide (H decreased from 1.11 to 0.13). After 12 wk incubation, H increased to 0.63 in the methyl bromide treated samples. PCA of PLFA profiles showed that microbial communites from methyl bromide treated soil may be different from other soils treated with other fumigants.

Agronomy Abstract p. 224, 1999.

MICROCOSM ENRICHMENT OF FUMIGANT-DEGRADING SOIL MICROBIAL COMMUNITIES

M. Ibekwe, S.K. Papiernik, J. Gan, S.R. Yates, C.H. Yang and D. Crowley

DGGE profiles of PCR amplified 16S rDNA genes were used to assess the diversity of fumigant-adapted microbial communities. Growth of microorganisms was stimulated by incubating soil with or without organic amendment and different fumigants in glass columns. After 6 months, stable population densities of fumigant degrading communities were established and a large percentage were able to grow on fumigant-containing minimal medium plates. DGGE provided a fast evaluation of the distribution of amplified sequence types. The banding patterns from samples treated with organic amendment and fumigants were different from the control soil. Fragments from 26 individual DGGE bands were sequenced and compared to published 16S rRNA gene sequences. Our results suggest that application of organic amendment with fumigants may enhance growth of specific strains of bacteria that can increase the degradation rate of these compounds.

Agronomy Abstract p. 225, 1999.

IMPACT OF FUMIGANTS OF STRUCTURAL DIVERSITY OF AMMONIA-OXIDIZING BACTERIA

A.M. Ibekwe, S.K. Papiernik, J. Gan and S.R. Yates

Ammonia-oxidizing bacteria perform the first step in nitrification, which is known to be the rate-limiting step. To determine the effects of fumigants on nitrification rates and on community structure of ammonia-oxidizing bacteria, a microcosm approach was used in a 12 wk incubation experiment with soil that has no history of fumigation. The data suggest that nitrification was significantly disrupted after the first 7 d of the experiment. The effects were more severe with MeBr and MITC treatments than with 1,3-D and chloropicrin. The community structures of ammonia-oxidizing bacteria from the four treatments were compared by 16S rDNA PCR-DGGE analysis using primers that target this group. DGGE analysis of ammonia oxidizing bacteria from the four treatments revealed two identical bands with the primers, indicating spatial and temporal reproducibility after 12 wk. Sequencing of these clones revealed the presence of only Nitrosospira-like sequences. Southern blot analysis with the primers showed a very bright band of correct size with Nitrosospira probe in all the treatments after 8 wk, but not with Nitrosomonas probe.

Agronomy Abstract p. 256, 2000.

SPATIAL AND TEMPORAL DISTRIBUTION OF SOIL BORON CONTENT IN SELECTED IRRIGATED SOILS

J.A. Jobes, P.J. Shouse, S. Goldberg, J.E. Ayars and R. Soppe

Boron is an important micro-nutrient for plant growth, but the range between sufficiency and toxicity is reportedly narrow for agronomic crops. We surveyed several soils using various extraction methods to determine the spatial and temporal distributions of extractable Boron and salinity in California. The extraction methods gave similar trends, but the absolute concentrations were quite different. The relationships among the extractable Boron and plant uptake are being studied and results will be presented. Our geostatistical results indicate that the overall variance in Boron concentration is higher at shallow depths and lower at depth in soils that have shallow groundwater. Boron concentrations are correlated with salinity and the correlations were stronger with depth. Boron and salinity were relatively constant during our study (3-5 years).

Agronomy Abstract p. 217, 2000.

CHARACTERIZATION AND MEASUREMENT OF THE UNSATURATED POROUS MEDIA

F.J. Leij and M. Th. van Genuchten

Quantifying and elucidating fluid flow in partially saturated porous media remains an important challenge, with many scientific and management applications. This paper contains a synopsis of theoretical and experimental methods to study and estimate the hydraulic properties of unsaturated media. Our main purpose is to provide a framework for the Proceedings of the workshop "Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media." We first discuss some of the problems related to the characterization and modeling of fluid flow in unsaturated media, as well as recent progress in this area. Subsequently we will peruse contributions to the workshop along five broad themes: (i) pore-scale phenomena, including those for multifluid systems, (ii) direct measurement methods, (iii) inverse modeling, (iv) indirect methods, and (v) other contributions pertaining to recent flow and transport research. We conclude by listing a number of topics in need for further investigation; this following a similar list compiled after the previous workshop [*van Genuchten and Leij,* 1992].

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media, Part* 1, pp. 1-12, University of California, Riverside, CA, 1999.

PRINCIPLES OF SOLUTE TRANSPORT

F.J. Leij and M. Th. van Genuchten

The chapter reviews elementary aspects of solute transport in soils. Such transport has traditionally been described with the convection-dispersion equation (CDE). This equation incorporates two constitutive transport processes: (i) movement as a result of liquid flow and (ii) spreading as a result of known and unknown processes such as diffusion and small scale variations in the water flow velocity. In Part II we will review several modes of solute transport: convection, diffusion in free liquids and subsequently in soils, mechanical dispersion, and (hydrodynamic) dispersion. The governing transport equation is derived from mass balance principles in Part III. Many other processes may affect the movement and fate of solutes in soils. Part IV is devoted to the important process of linear and nonlinear solute adsorption.

In: J. van Schilfgaarde and W. Skaggs (ed.), *Drainage in Agriculture*, Chapter 9, pp. 331-359, Agronomy No. 38, Am. Society of Agronomy, Madison, WI, 1999.

SOLUTE TRANSPORT

F.J. Leij and M. Th. van Genuchten

The topic of solute transport in soils was reviewed in a general manner in this chapter. The description focused on the use of the advection-dispersion equation (ADE). The key concepts for transport according to the ADE were introduced with a brief discussion of how to determine transport parameters. The development and, especially, the application of process-based models to field- and laboratory-scale transport is likely to remain of great importance for studying and managing the fate and movement of chemicals in soils. Such models are attractive because they may yield information for a much wider range of conditions than can be achieved through regular experimental investigations. Most attention hence was paid to formulating transport models.

The successful application of a transport model requires that the water flow regime can be quantified. This can usually be done prior to solving the transport problem but in some cases the solute regime will affect the soil hydraulic properties. Diffusion, which is included in the dispersive term of the ADE, may become an important mechanism for solute movement in the liquid phase in soils with low water velocities. The difference in terminology regarding tortuosity was brought up in section 6.2. 1. 1, which also contained some background on diffusion measurements. Mechanical dispersion, or simply dispersion, has been widely discussed in the literature and an introduction was provided to the subject in section 6.2.1.2. The ADE was subsequently formulated using the principle of mass conservation. The movement of the solute may be greatly affected by adsorption onto the solid phase. Linear and nonlinear adsorption were therefore discussed in the context of solute transport modeling. Multicomponent transport was very briefly reviewed in section 6.2.4 because the behavior of a single solute species in a natural soil will usually be affected by many different components and a variety of chemical processes. Particularly for flow and transport in natural soils, the ADE should account for nonequilibrium transport. Nonequilibrium transport may occur during solute movement in structured media with bypass flow or for kinetic solute adsorption. Section 6.2.5 contains the mathematical formulation for a bi-continuum nonequilibrium model as well as an analytical solution and application for solute input to a structured soil.

Analytical and numerical modeling of the ADE was discussed in section 6.3. This section specified relevant concentration modes as well as boundary and initial conditions needed to complete the mathematical formulation of the transport problem. Analytical solutions may be useful to gain further insight in the transport model, to study solute behavior in soils over large temporal or spatial scales, to evaluate numerical models, and to determine model parameters from results of well-controlled experiments. Various transformations were provided that facilitate such solutions and selected equilibrium and nonequilibrium solutions were provided. Applications of these solutions were also illustrated. Time moments were defined for describing the breakthrough and spreading of a solute in soils as an alternative to the standard solution of the governing partial differential equations for solute transport. A general overview was given of numerical solution procedures for the ADE with a qualitative outline was included of the common methods of finite differences and finite elements. The finite difference method is attractive because of its simplicity while the finite element method is better able to handle a solution domain with an irregular geometry or nonuniform transport properties. The effect of the numerical scheme on the predicted concentration profile was shown for a relatively large column Peclet number.

Stochastic modeling of (field-scale) transport of chemicals in soils is increasingly receiving

attention in the literature because of soil heterogeneity, limitations in the invoked transport models, and uncertainty in the estimated transport parameters. The stream tube concept is one of a few stochastic approaches that can be applied to actual problems. The stream-tube model simplifies the heterogeneity of the soil and allows the use of analytical techniques to estimate the averaged concentration across the field as well as its variation for specified probability density functions for selected transport parameters.

In: M. Sumner (ed.), *Handbook of Soil Science*, Chapter 6, pp. A183-1227. CRC Press, Boca Raton, FL, 1999.

RELATIONSHIP BETWEEN PARTICLE-SIZE DISTRIBUTION AND SOIL WATER RETENTION

L.M. Arya, F.J. Leij and M. Th. van Genuchten

The water retention characteristic of a soil is intimately related to its particle-size distribution and packing density. Translation of the particle-size distribution into a corresponding soil water characteristic curve involves converting particle sizes to equivalent pore radii, and solid mass fractions to equivalent pore volumes. Since particle sizes are expressed in diameters of equivalent spheres, the simplest geometrical structure is one in which uniform-size spherical particles are arranged in cubic close-packed assemblages. The pore lengths and pore radii in such hypothetical cubic structures can be scaled to those in corresponding natural structures, made up of the same solid mass but consisting of nonspherical particles in random orientations. The procedure involves measuring the natural pore length in units of the number of spherical particles, with each particle contributing a length equal to its diameter. Thus, if the *i*th particle-size fraction consists of n_i spherical particles of radius R_i, tracing the pore length generated by the fraction solid mass, when arranged in a natural state of packing, would require n_i^{α} particles of radius R_i. The concept first developed by *Arya and Paris* [1981] treated α as a universal constant. In this study, α is defined for individual particle-size fractions according to $\alpha_i = (\log N_i / \log n_i)$, where $N_i = n_i^{\alpha}$. Our study, applied to five textural classes, shows that $\log N_i$ is related to $\log n_i$ following a logistic growth equation and that α is not a constant; rather α decreases with increasing particle size. However, the decrease in α is relatively small from clay- to medium sand-size particles. A sharp decrease in α occurs only for relatively coarse particles. The new formulation for α and the constant average values calculated for various textural classes were evaluated for 23 soils, presenting a range of particle-size distribution, bulk density, and organic matter content. The general shape of the soil water characteristic curves could be predicted fairly well with both forms of α, with the predicted pressures differing from the experimental pressures by no more than what might be expected between random samples of the same soil. However, the single-value average α consistently predicted lower pressures in the wet range and higher pressures in the dry range, thereby showing a pronounced bias in the predictions. The new formulation for α produced closer agreement with the experimental data, and no bias was observed.

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media*, Part 1, pp. 931-946, University of California, Riverside, CA, 1999.

RELATIONSHIP BETWEEN THE HYDRAULIC CONDUCTIVITY FUNCTION AND THE PARTICLE-SIZE DISTRIBUTION

L.M. Arya, F.J. Leij, P.J. Shouse and M. Th. van Genuchten

We present a model to compute the hydraulic conductivity, K, as a function of water content, θ, directly from the particle-size distribution (PSD) of a soil. The model is based on the assumption that soil pores can be represented by equivalent capillary tubes and that the water flow rate is a function of pore size. The pore-size distribution is derived from the PSD using the Arya-Paris model. Particle-size distribution and $K(\theta)$ data for 16 soils, representing several textural classes, were used to relate the pore flow rate and the pore radius according to $q_i = cr_i^x$ where q_i *is* the pore flow rate ($cm^3\ s^{-1}$) and r_i is the pore radius (cm). Log c varied from about -2.43 to about 2.78, and x varied from $\approx$ 2.66 to $\approx$4.71. However, these parameters did not exhibit a systematic trend with textural class. The model was used to independently compute the $K(\theta)$ function, from the PSD data for 16 additional soils. The model predicted $K(\theta)$ values from near saturation to very low water contents. The agreement between the predicted and experimental $K(\theta)$ for individual samples ranged from excellent to poor, with the root mean square residuals (RMSR) of the log-transformed $K(\theta)$ ranging from 0.616 to 1.603 for sand, from 0.592 to 1.719 for loam, and from 0.487 to 1.065 for clay. The average RMSR for all textures was 0.878.

Soil Sci. Soc. Am. J. 63(5):1063-1070, 1999.

SCALING PARAMETER TO PREDICT THE SOIL WATER CHARACTERISTIC FROM PARTICLE-SIZE DISTRIBUTION DATA

L.M. Arya, F.J. Leij, M. Th. van Genuchten and P.J. Shouse

The Arya-Paris model is an indirect method to estimate the soil water characteristic from particle-size data. The scaling parameter, α, in the original model was assumed constant for all soil textures. In this study, at is defined as $\alpha = (\log N_i/\log n_i)$, where n_i is the number of spherical particles in the ith particle-size fraction (determined by the fraction solid mass, w_i, and mean particle radius, R_i) and N_i *is* the number of spherical particles of radius R_i, required to trace the pore length generated by the same solid mass in a natural structure soil matrix. An estimate for log N_i was obtained by either relating log N_i to log n_i using a logistic growth equation or by relating log N_i linearly to log (w_i/ R_i^3) based on the similarity principle. For any given texture, both approaches showed that *a* was not constant but decreased with increasing particle size, especially for the coarse fractions. In addition, α was also calculated as a single-value average for a given textural class. The three formulations of α were evaluated on 23 soils that represented a range in particle-size distribution, bulk density, and organic matter content. The average α consistently predicted higher pressure heads in the wet range and lower pressure heads in the dry range. The formulation based on the similarity principle resulted in bias similar to that of the constant α approach, whereas no bias was observed for the logistic growth equation. The logistic growth equation implicitly accounted for bias in experimental procedures, because it was fitted to log N_i values computed from experimental soil water characteristic data. The formulation based on the similarity principle is independent of bias that might be inherent in experimental data.

Soil Sci. Soc. Am. J. 63(3):510-519, 1999.

STOCHASTIC MODEL FOR POST-TILLAGE SOIL PORE SPACE EVOLUTION

D. Or, F.J. Leij, V. Snyder and T.A. Ghezzehei

Tillage operations disrupt surface layers of agricultural soils, creating a loosened structure with a substantial proportion of interaggregate porosity that enhances liquid and gaseous exchange properties favorable for plant growth. Unfortunately, such desirable soil tilth is structurally unstable and is susceptible to change by subsequent wetting and drying processes and other mechanical stresses that reduce total porosity and modify pore size distribution (PSD). An ability to model post-tillage dynamics of soil pore space and concurrent changes in hydraulic properties is important for realistic predictions of transport processes through this surface layer. We propose a stochastic modeling framework that couples the probabilistic nature of pore space distributions with physically based soil deformation models using the Fokker-Planck equation (FPE) formalism. Three important features of soil pore space evolution are addressed: (1) reduction of the total porosity, (2) reduction of mean pore radius, and (3) changes in the variance of the PSD. The proposed framework may be used to provide input to hydrological models concerning temporal variations in near-surface soil hydraulic properties. In a preliminary investigation of this approach we link a previously proposed mechanistic model of soil aggregate coalescence to the stochastic FPE framework to determine the FPE coefficients. An illustrative example is presented which describes changes in interaggregate pore size due to wetting-drying cycles and the resulting effects on dynamics of the soil water characteristic curve and hydraulic conductivity functions.

Water Resour. Res. 36(7):1641-1652, 2000.

PREDICTING UNSATURATED HYDRAULIC CONDUCTIVITY FUNCTIONS FROM PARTICLE SIZE DISTRIBUTIONS

L.M. Arya, F.J. Leij, P.J. Shouse and T.H. Skaggs

We present a model to compute the hydraulic conductivity-water content function directly from the particle size distribution of a soil. The model is based on the assumption that soil pores can be represented by equivalent capillary tubes and that the water flow rate is a function of pore size. Particle size distribution and conductivity data for 16 soils were used to relate the pore flow rate to the pore radius. Parameters of this logarithmic function did not exhibit a systematic trend with textural class. The model was used to compute the hydraulic conductivity for 16 additional soils. The agreement between the predicted and the experimental values for individual samples ranged from excellent to poor with the root mean square residuals of the log transformed conductivity ranging from 0.62 to 1.60 for sands, from 0.59 to 1.72 for loams and from 0.49 to 1.07 for clays. The average root mean square residuals for all textures was 0.88.

Agronomy Abstract p. 193, 1999.

SCALING HYDRAULIC PROPERTIES OF A MACROPOROUS SOIL

B.P. Mohanty

Macroporous soils exhibit significant differences in their hydraulic properties for different pore domains. Multimodal hydraulic functions may be used to describe the characteristics of multiporosity media. I investigated the usefulness of scaling to describe the spatial variability of hydraulic conductivity ($K(-h)$) functions of a macroporous soil in Las Nutrias, New Mexico. Piecewise-continuous hydraulic conductivity functions suitable for macroporous soils in conjunction with a hybrid similar media-functional normalization scaling approach were used. Results showed that gravity-dominated flow and the related hydraulic conductivity ($K(-h)$) functions of the macropore region are more readily scalable than capillary-dominated flow properties of the mesopore and micropore regions. A possible reason for this behavior is that gravity-dominated flow in the larger pores is mostly influenced by the pore diameter, which remains more uniform as compared to tortuous mesopores and micropores with variable neck and body sizes along the pore length.

Water Resour. Res. 35(6):1927-1931, 1999.

SOIL MOISTURE CONTENT AT DEEPER DEPTHS - SGP971 OKLAHOMA

B.P. Mohanty, P.R. Houser, P.J. Shouse and M. Th. van Genuchten

The soil moisture content at deeper depths is important for global water balance calculations. While recent developments of remote sensing technologies seem more tractable for estimating the soil moisture content (SMC) of relatively shallow depths (0-5 cm) over large land areas, numerical variably-saturated flow modeling provides an attractive tool for extrapolating surface SMCs to deeper depths. In this paper we show results of HYDRUS model simulations at several locations across the Southern Great Plains Hydrology Experiment 1997 (SGP97) region. HYDRUS is based on the one-dimensional Richards equation for variably-saturated flow, and the van Genuchten functions for soil water retention and unsaturated hydraulic conductivity. The model can handle both flux- and head-type boundary conditions, root water uptake, and temperature dependent as well as hysteretic soil hydraulic properties. Atmospheric forcing such as transient precipitation (flux) provide the top boundary condition for water flow simulations in one-dimensional soil pedons. Observed gravimetric SMC data measured during SGP97 at deeper depths (up to 1 m) at several locations using a truck-mounted Giddings probe were used to test the model predictions. A reasonable match between observed and simulated SMCs were noted at several quarter sections with different soil textures. SMCs at deeper depths in the fields with grass/wheat cover were equally well predicted as bare land. Contrary to common perception, the one-dimensional model even performed reasonably well at the sampling points having moderate slopes.

Proc. 14th Conf. On Hydrology, American Meteorological Society, Boston, MA, pp. 141-142, 1999.

SCALING BEHAVIOR OF NEAR-SATURATED HYDRAULIC CONDUCTIVITY

B.P. Mohanty and P.J. Shouse

The near-saturated hydraulic conductivity function, $K(h)$, is critical for describing flow in macropores and other structural voids. The usefulness of similar media scaling and functional normalization to describe the near-saturated hydraulic conductivity function, $K(h)$, measured *in situ* at 296 spatial locations across a heterogenous agricultural field was tested. Disc (ponded and tension) infiltrometers were used to measure $K(h)$ at different field positions (corn row, no traffic inter-row, and traffic inter-row) cutting across different soil types (Nicollet and Clarion loam derived from glacial till material). The $K(h)$ data ranged several orders of magnitude for different field positions and soil types and were found to be statistically different between different field positions. Using a Gardner type $K(h)$ function, relative hydraulic conductivity values, and a hybrid of similar media scaling and functional normalization concepts all disc infiltrometer data sets were coalesced to a single reference curve. A novel finding is that saturated hydraulic conductivities (K_{sat}) could be successfully used as the scale factor for the near-saturated $K(h)$ functions (e.g., 0-15 cm soil water tension) under all field positions and soil types at the experimental field.

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media*, Part 1, pp. 1415-1424, University of California, Riverside, CA, 1999.

INTER-COMPARISON OF THREE METHODS FOR MEASURING SOIL MOISTURE DURING SGP97

R.L. Elliott, P.R. Houser and B.P. Mohanty

Soil moisture plays a major role in the physics of the soil-plant-atmosphere continuum. Soil moisture is a key factor in plant growth, evapotranspiration, soil water and heat flux, and the hydrologic and surface energy balances. The water content of soils influences rainfall-runoff relationships, flooding potential, ground water recharge, and biological processes. Effective drought assessment and irrigation management are dependent on soil moisture information. round-based soil-moisture measurement was an integral part of the Southern Great Plains 1997 (SGP97) Hydrology Experiment, and was particularly focused on providing "ground truth" information for remote sensing techniques (Jackson, 1999; Humes et al., 1999). Near-surface and profile measurements of soil moisture were made using a variety of techniques and instrumentation. These data were inter-compared and quality assured to maximize their value in meeting the Experiment's objectives.

Our study used three independent sources of SGP-97 soil moisture information: (1) surface and profile measurements of gravimetric water content; (2) measurements of volumetric water content using time domain reflectometry; and (3) heat dissipation sensors for measuring soil matric potential, installed at four depths. Each technique yields a different unit of measurement for soil moisture, so conversions must be made before the data can be inter-compared.

Reprints, 14th Conference on Hydrology, pp. 178-181. American Meteorological Society, Boston, MA. 1999.

GROUND-BASED INVESTIGATION OF SOIL MOISTURE VARIABILITY WITHIN REMOTE SENSING FOOTPRINTS DURING SGP97: FIRST RESULTS

J.S. Famiglietti, J.A. Devereaux, C. Laymon, T. Tsegaye, P.R. Houser, T.J. Jackson
S.T. Graham, M. Rodell and B.P. Mohanty

The Southern Great Plains 1997 (SGP97) Hydrology Experiment was the largest airborne L-band passive microwave mapping mission of surface soil moisture to date. Located in a 50 km by 250 km strip of central Oklahoma, soil moisture was mapped nearly every day between June 18 and July 18, 1997, at a 1-km ground resolution. Since the hydrologic community anticipates that the SGP97 sensor, the ESTAR (Electronically Scanned Thinned Array Microwave Radiometer), will ultimately provide 25-50 km resolution global soil moisture monitoring from a space-based platform, the goal of this investigation was to more rigorously characterize ESTAR performance than would be possible with a standard, ground-truth sampling plan typically associated with soil moisture remote sensing experiments. Specifically, the goal of this field investigation was to provide, to the degree possible given the constraints of the SGP97 experiment, accurate estimates of the mean, variance, and frequency distributions of surface moisture content within selected, representative, sensor footprints. Ongoing research will compare our observations to ESTAR-derived soil moisture field values, with implications for ESTAR accuracy and the underlying variability that remote sensing cannot record explicitly (i.e. the variance and frequency distributions).

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media, Part* 1, pp. 563-570, University of California, Riverside, CA, 1999.

THE SPATIAL-TEMPORAL STRUCTURE OF U.S. SOUTHERN GREAT PLAINS SOIL MOISTURE: AN ANALYSIS OF IN-SITU PROFILE OBSERVATIONS

P.R. Houser and B.P. Mohanty

Soil moisture links the hydrologic cycle and the energy budget of land surfaces by regulating the partitioning of surface radiative energy between latent and sensible eat fluxes. Therefore, accurate assessment of the spatial and temporal variation of soil moisture is important for the study, understanding, and management of surface biogeophysical processes. However, soil moisture exhibits a high degree of variability whose cause has been elusive, but is thought to be determined by heterogeneity in soil properties, vegetation, topography, water table depth, precipitation, and other meteorological factors. Understanding and assessment of these variations across a range of scales will enable the definition of the vertical and horizontal soil moisture error correlation structures which are essential for soil moisture assimilation studies.

During the Southern Great Plains Experiment (SGP97) (Jackson, 1997), soil moisture, soil properties, vegetation characteristics, and meteorological information was measured for a period of 30 days at a wide range of scales ranging from 1 m to 250 km. The preliminary analysis of these observations is presented here. This analysis is focused on the calibration of soil moisture measurements and assessment of the spatial and temporal structure of soil moisture at El Reno, Oklahoma.

The Delta-T frequency domain reflectometer Theta Probes used in this study to measure near-surface soil moisture showed little inter-probe variability, and some soil dependence. The ESI time domain reflectometer Moisture Point Probes used to measure profile soil moisture over several depth ranges generally overestimate soil moisture, with a decreasing sensitivity with depth. It is suspected that soil heterogeneity and compression adversely influence both the Theta and Moisture Point Probes. In the analysis of near-surface soil moisture sampling error, it was found that both average sampling error, and soil moisture variability increase in drier soil. Sampling error is also generally scale independent. There is a high degree of uncorrelated soil moisture spatial variability both horizontally and vertically, although some spatial structure is evident.

Preprints, 14th Conference on Hydrology, pp. 204-205, American Meteorological Society, Boston, MA, 1999.

SPATIO-TEMPORAL EVOLUTION AND TIME STABILITY OF SOIL MOISTURE CONTENT DURING THE SGP97 HYDROLOGY EXPERIMENT

B.P. Mohanty and T.H. Skaggs

Air-borne passive microwave remote sensors measure soil moisture at the footprint scale, a scale of several hundred square meters or kilometers that encompasses different characteristic combinations of soil, topography, vegetation, and climate. Studies of within-footprint variability of soil moisture are needed to determine the factors governing hydrologic processes and their relative importance, as well as to test the efficacy of remote sensors. We used gridded ground-based impedance probe water content date and aircraft mounted Electronically Scanned Thinned Array Radiometer (ESTAR) pixel-average soil moisture data to investigate the spatio-temporal evolution and time stable characteristics of soil moisture in three selected (LW03, LW13, LW21) footprints from the Southern Great Plains 1997 (SGP97) Hydrology Experiment. Better time stable features were observed within a footprint containing sandy loam soil than within two pixels containing silty loam soil. Additionally, flat topography with split wheat/grass land cover produced the largest spatio-temporal variability and the least time stability in soil moisture patterns. A comparison of ground-based and remote sensing data showed that ESTAR footprint-average soil moisture was well calibrated for the LW03 pixel with sandy loam soil, rolling topography, and pasture land cover, but improved calibration is warranted for the LW13 (silty loam soil, rolling topography, pasture land) and LW21 (silty loam soil, flat topography, split vegetation of wheat and grass land with tillage practice) pixels. Footprint-scale variability and associated nonlinear soil moisture dynamics may prove to be critical in the regional-scale hydro-climatic models.

Am. Geophys. Union, p. 553, 2000.

EVOLUTION OF SOIL MOISTURE SPATIAL STRUCTURE IN A MIXED VEGETATION PIXEL DURING THE SOUTHERN GREAT PLAINS 1997 (SGP97) HYDROLOGY EXPERIMENT

B.P. Mohanty, J.S. Famiglietti and T.H. Skaggs

Different factors contribute to soil-moisture variability at different space scales and time scales, including soil properties, topography, vegetation, land management, and atmospheric forcings, such as precipitation and temperature. Field experiments supported by adaptive geostatistical and exploratory analysis, including categorical elimination of different governing factors, are needed to bring new insight to this important hydrologic problem. During the Southern Great Plains 1997 (SGP97) Hydrology Experiment in Oklahoma, we investigated the within-season (intra-seasonal) spatiotemporal variability of surface (0 - 6 cm depth) soil moisture in a. quarter section (800 m x 800 m) possessing relatively uniform topography and soil texture but variable land cover. Daily soil moisture measurements were made between June 22 and July 16 using portable impedance probes in a regular 7 x 7 square grid with 100-m spacings. Initially, the land cover was split between grass and wheat stubble; row tilling on June 27 converted the wheat stubble to bare ground. Geostatistical and median polishing schemes were used to analyze the within-season evolution of the spatial structure of soil moisture. The effects of daily precipitation, variable land cover, land management, vegetation growth, and micro-heterogeneity including subgrid-scale variability were all visible in the analysis. The isotropic spatial correlation range for soil moisture varied between <100 m (for nugget and subgrid-scale variability) and >428 m (for spherical and Gaussian models) within the 4-week-long SGP97 experiment. The findings will be useful for assessing remotely sensed soil moisture data collected during the SGP97 Hydrology Experiment in mixed vegetation pixels.

Water Resour. Res. 36(12):3675-3686, 2000.

ANALYSIS AND MAPPING OF FIELD-SCALE SOIL MOISTURE VARIABILITY USING HIGH-RESOLUTION, GROUND-BASED DATA DURING THE SOUTHERN GREAT PLAINS 1997 (SGP97) HYDROLOGY EXPERIMENT

B.P. Mohanty, T.H. Skaggs and J.S. Famiglietti

Soil moisture is an important state variable in the hydrologic cycle, and its spatiotemporal distribution depends on many geophysical processes operating at different spatial and temporal scales. To achieve a better accounting of the water and energy budgets at the land-atmosphere boundary, it is necessary to better understand the spatiotemporal variability of soil moisture under different hydrologic and climatic conditions and at different hierarchical space scales and timescales. During the Southern Great Plains 1997 (SGP97) Hydrology Experiment the 0-6 cm soil water content was measured on consecutive afternoons at 400 locations in a small, gently sloping range field (Little Washita field site 07). The soil moisture measurements were made using portable impedance probes. Spatiotemporal data analyses of the two sampling events showed a significant change in the field variance but a constant field mean, suggesting moisture was redistributed by (differential) base flow, evapotranspiration, and condensation. Among the different relative landscape positions (hilltop, slope, valley) the slope was the largest contributor to the temporal variability of the soil moisture content. Using a sequential aggregation scheme, it was observed that the relative position influencing the field mean and variance changed between the two sampling events, indicating time instability in the spatial soil moisture data. Furthermore, high-resolution (impedance probe) sampling and limited (gravimetric) sampling gave different field means and variances.

Water Resour. Res. 36(4):1023-1031, 2000.

WATER AND CHLORIDE TRANSPORT IN A FINE-TEXTURED SOIL: FIELD EXPERIMENTS AND MODELING

D. Ventrella, B.P. Mohanty, J. Šimůnek, N. Losavio and M. Th. van Genuchten

Numerical models are being used increasingly to simulate water and solute movement in the subsurface for a variety of applications in research and soil/water management. Although a large number of models of varying degrees of complexity have been developed over the years, relatively few have been tested under field conditions. We tested the performance of the HYDRUS-1D computer model to simulate variably saturated water flow and chloride transport in a fine-textured Italian soil subject to a fluctuating saline groundwater table. The model was also used for estimating solute transport parameters using an inverse optimization scheme. Our results indicate that including the effects of immobile water produced better predictions of chloride transport compared with the traditional convection-dispersion transport approach. Including anion exclusion as well did not improve the model predictions appreciably. Occasional deviations between model prediction and field observation were attributed to unrepresented lateral groundwater flow processes and to preferential flow through macropores or other structural voids. The HYDRUS-ID model was found to be very useful for analyzing the relatively complex flow and solute transport processes 'at our field site and for estimating model parameters using inverse procedures.

Soil Sci. 165:624-631, 2000.

MODELING PREFERENTIAL FLOW IN A TILE-DRAINED FIELD USING DOUBLE-HUMP TYPE K(H) FUNCTIONS

B.P. Mohanty

Preferential flow under saturated as well as near-saturated conditions through macropores, cracks, and other non-matrix domains that coexist with the soil matrix domain, has been found to be very common in structured field soil. Disc infiltrometry methods involving ponded and tension infiltrometers in conjunction with multi-step outflow methods could provide a more complete *K-h* function for field soils. Results of a flow-transport field study near Las Nutrias, New Mexico will be summarized in this presentation. A novel finding of this study is the (bimodal) double-hump feature of the measured *K-h* function, which was modeled using piecewise-continuous functions. Incorporating the bimodal *K-h* functions in a numerical model (CHAIN_2D) improved the flow and transport predictions at the field site. Furthermore, *K-h* functions for gravity-dominated flow regions were found to be more readily scalable than *K-h* functions for capillary-dominated flow regions.

Agronomy Abstract p. 194, 1999

SORPTION OF FUMIGANTS TO AGRICULTURAL FILMS

S.K. Papiernik, J. Gan, J.A. Knuteson and S.R. Yates

Plastic tarps are often used in soil fumigation to contain chemicals in the soil to increase efficacy and decrease emissions of fumigant vapors. This research has shown that plastic films have a significant capacity to sorb fumigant vapors and that the sorption is largely reversible. We tested three agricultural films (polyethylene and two high barrier films) with four soil fumigants (methyl bromide, chloropicrin, 1,3-dichloropropene, and propargyl bromide, a potential alternative to methyl bromide). We observed significant sorption of all fumigants to all the films at field relevant concentrations. Partition coefficients (sorbed/ vapor-phase concentration) ranged from <1 dm^3/m^2.film for methyl bromide to ~200 dm^3/m^2 film for chloropicrin. Sorption isotherms were linear, indicating that the film may be a large sink for fumigant vapors. Sorption of most fumigants was very rapid, with the bulk of the sorption occurring within the first few minutes of contact. Desorption was also rapid, with most desorption occurring within minutes after the film samples were removed to fresh air. First-order rate constants for desorption were -0.5 to 1.5 min^{-1}. Sorption/desorption may be important in reducing emissions and determining worker exposure and should be considered in measurements involving agricultural films.

Environ. Sci. Technol. 33:1213-1217, 1999.

A NEW METHOD FOR ESTIMATING THE PERMEABILITY OF PLASTIC FILMS TO FUMIGANT VAPORS

S.K. Papiernik and S.R. Yates

When greenhouse and field soils are fumigated, the soil surface is often covered with a plastic tarp to reduce loss of the chemical via volatilization. Low- or high-density polyethylene tarps (LDPE or HDPE) are commonly used; however, these films have been reported to have signficant permeability to methyl bromide (MeBr) and other soil fumigants. Plastic films that have reduced permeability to soil fumigants, particularly MeBr, have been developed in response to the call for management practices that reduce emissions and maintain or increase the efficacy of soil fumigants. To assist in the development of these management practices, a rapid, accurate method to measure the permeability of plastic films to soil fumigants is needed.The permeability of plastic films to gaseous solutes is due to diffusion and is thought to occur by the solute dissolving into the surface of the film, followed by the diffusion through the film and evaporation from the opposite film surface. This paper describes a new method for estimating the mass transfer coefficient of gases diffusing through plastic films. Unlike currently-used methods, which use a flow-through chamber under steady state conditions, the transfer of fumigant across a film was determined in a static chamber. This method was used to measure the permeability of HDPE to MeBr, 1,3-dichloropropene (1,3-D), and chloropicrin.

Permeability cells were fabricated from stainless steel cylindrical stock of 12 cm ID. Cells were constructed in two halves, each approximately 4 cm long, sealed on one end by soldering a stainless steel plate to the column. Additional cells for the testing of low permeability films were 12 cm (H) x 1 cm (each half). A piece of the plastic film to be tested was placed between the two cell halves and the cell halves sealed together to provide a gas tight system. Sampling ports were constructed from brass fittings and were installed at the midpoint of each cell half.

Vapor was spiked on one side of the film (source chamber), and the gas-phase concentration on each side of the film was monitored until concentrations in the source chamber and receiving chamber were equal. MeBr, 1,3-D, and chloropicrin were spiked to separate cells (3 replicates per fumigant). Gas-tight syringes were used to collect vapor samples from each chamber at various times throughout the course of the experiment. Samples were placed in headspace vials and analyzed using headspace GC-ECD.

Proceedings of the 1999 *Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reductions.* November 1-4, San Diego, CA. 3 0:1-3, 1999.

PRESENCE AND BIOTRANSFORMATION OF THREE HETEROAROMATIC COMPOUNDS COMPARED TO AN AROMATIC HYDROCARBON

J. Hellou, J. Leonard, J. Meade, S. Sharpe, J. Banoub, S.K. Papiernik, L. Eglinton and J. Whelan

The presence of nitrogen, oxygen and sulfur containing aromatic compounds, namely carbazole, dibenzofuran. dibenzothiophene and their alkylated derivatives was investigated in potential environmental sources of these compounds. The persistence vs biodegradation of the parental heteroaromati c compounds was determined using bacterial consortia collected from three marine beaches from coastal Newfoundland. Experiments were performed at 25 and 4°C and bacterial populations derive from differently contaminated environments. In separate studies, rainbow trout, Salmo gardneiri, were exposed to PACs through their diet and the bioelimination of crlucuronide and sufate conjugates followed in the gall bladder bile after a single and during continuous exposure. Comparison was done between the presence and fate of the three heterocyclic PACs and that of fluorene. a PAH counterpart with similar structure and physicalchemical properties. The tissue distribution of the PACs (not presented). provides information on the potential narcotic and/or reproductive effect of the unreacted compounds and the metabolites on the potential toxicity of the oxidation products.

Polycyclic Aromatic Compounds 14:221-230, 1999.

A REVIEW OF IN SITU MEASUREMENT OF ORGANIC COMPOUND TRANSFORMATION IN GROUNDWATER

S.K. Papiernik

Laboratory assessments of the rate of degradation of organic compounds in groundwater have been criticized for producing unrepresentative results. The potential for organic compounds to be transformed in groundwater has been measured using in situ methods, which avoid problems of attempting to duplicate aquifer conditions in the laboratory. In situ assessments of transformation rates have been accomplished using transport studies and in situ microcosms (ISMs); a review of these methods is given here. In transport studies, organic solutes are injected into an aquifer and the concentrations are monitored as they are transported downgradient. The change in mass of a solute is determined by the area contained under the breakthrough curve (plot of concentration versus time). ISMs isolate a portion of the aquifer from advective flow and act as in situ batch reactors. Experiments using ISMs involve removing water from the ISM, amending it with the solutes of interest, re-injecting the amended water, and monitoring the solute concentrations with time. In both transport and ISM studies, the loss of organic solutes from solution does not allow for a distinction between sorptive, abiotic and biotic transformation losses. Biological activity can be chemically suppressed in ISMs and the results from those experiments used to indicate sorption and abiotic loss. Transformation products may be monitored to provide additional information on transformation mechanisms and rates.

Third SETAC World Congress, May 21-25, Brighton, UK, 2000.

PRODUCTS OF PROPARGYL BROMIDE DEGRADATION IN SOIL

S.K. Papiernik, J. Gan, R. Dungan and S.R. Yates

Propargyl bromide (C3H3Br; PrBr) is being investigated for its potential to partially replace methyl bromide (MeBr) as a soil finnigant. Information on its environmental fate, including mechanisms of degradation in soil, is required to evaluate PrBr's capacity for sustained usage. We have conducted a number of studies on the degradation on PrBr in soil, and monitored the formation of some of the products of PrBr degradation in soil and water.

Primary alkyl halides, including MeBr and PrBr react via nucleophilic substitution. This reaction mechanism imparts broad-spectrum toxicity through alkylation of nucleophilic groups in amino acids and peptides. All known mechanisms of PrBr and MeBr degradation in soil and water result in the formation of Br^-. Analysis of additional degradation products gives information on the mechanism of transformation.

Proceedings of the 2000 *Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reductions.* November 6-9, Orlando, FL. 27-1-3, 2000.

MECHANISM OF DEGRADATION OF METHYL BROMIDE AND PROPARGYL BROMIDE IN SOIL

S.K. Papiernik, J. Gan and S.R. Yates

The degradation of methyl bromide (MB) and propargyl bromide (PB) was investigated in soil and water to obtain information on the mechanism of degradation. It has been suggested that primary alkyl halides (including MB and the potential alternatives PB and methyl iodide) can undergo SN2 nucleophilic substitution with nucleophilic sites on soil organic matter (i.e., -NH2, -NH, -OH, -SH). The pattern of product formation observed in this study provides more direct evidence that fumigants that are primary alkyl halides can alkylate soil organic matter and that this may be a significant mechanism of degradation in soil. Degradation in water samples (hydrolysis) formed Br^- and the corresponding alcohol (propargyl alcohol from PB, methanol from MB) in equimolar amounts. The rate of hydrolysis was not significantly different from the rate of Br^- formation for both MB and PB. Degradation in two soils resulted in the formation of Br^-, but very little production of the corresponding alcohol, indicating that some mechanism other than hydrolysis must be occurring in the soil. Degradation of MB and PB was much more rapid in the higher organic-matter day loam soil than in the sandy loam soil. Spiking ^{14}C-labeled MB to soil resulted in the formation of nonextractable (soilbound) ^{14}C, which increased as the extractable ^{14}C decreased. Microbial oxidation was not significant in these soil samples, which were sterilized through autodaving and/or treatment with high concentrations of fumigants. These results provide further experimental evidence that MB, PB, and similar compounds can alkylate soil organic matter.

J. Environ. Qual. 29:1322-1328, 2000.

PERMEABILITY OF PLASTIC FILMS TO FUMIGANT VAPORS

S.K. Papiernik and S.R. Yates

When greenhouse and field soils are fumigated, the soil surface is often covered with a plastic tarp to reduce loss of the chemical via volatilization. Polyethylene tarps are commonly used; however, these films have significant permeability to methyl bromide and other soil fumigants. Films with lower permeability are being introduced. To develop management practices that protect the environment while providing adequate pest control, a rapid, accurate method to measure the permeability of plastic films to soil fumigants is needed. This paper describes a new method for estimating the mass transfer coefficient of agricultural films. The time-dependent transfer of fumigant across a membrane was determined in a static chamber; this method was used to measure the permeability of several plastic films to methyl bromide and other fumigants. This method, which requires a minimum of equipment, is especially useful as a screening tool in the development of new plastics, soil fumigants, and management practices.

Agronomy Abstract p. 33, 1999.

HERBICIDE-SALINITY INTERACTION EFFECTS ON PHYTOTOXICITY

S.K. Papiernik, C.M. Grieve, J. Gan, F.F. Ernst and S.R. Yates

The potential for irrigation water salinity to impact herbicide phytotoxicity to soybeans and six weed species was tested in a greenhouse study. Seeds were germinated and grown in individual pots irrigated with Hoagland's nutrient solution or simulated saline drainage water (EC 7dS/m) supplemented with nutrients. Imazethapyr (Pursuit, 4 oz/ac) and chlorimuron ethyl (Classic, 0.5 oz/ac) were applied post-emergence according to the label directives. Control plants were treated with the tank mix containing no herbicide. Plant growth was monitored for several weeks following herbicide application. In general, plants irrigated with saline water had a poorer germination rate, grew more slowly, and had a lower survival rate than plants grown using non-saline irrigation water. However, for some herbicide-plant type combinations, particularly with chlorimuron ethyl, no difference in post-treatment growth between the two water conditions was observed and salinized plants exhibited similar or higher survival rates. Strong differences in plant development were observed in herbicide-treated and control plants, with no observable effect of salinity. Herbicide treatment apparently disrupted the apical meristem of several species, including soybeans, with the subsequent formation of multiple shoots at the growing point; often one shoot became dominant and the plant partially recovered.

Agronomy Abstract p. 142, 2000.

DEVELOPMENT AND USE OF A HIERARCHICAL SET OF NEURAL NETWORK PEDOTRANSFER FUNCTIONS

M.G. Schaap, F.J. Leij and M. Th. van Genuchten

Pedotransfer functions (PTFs) are increasingly being used to obtain soil hydraulic characteristics for local, regional and global scale hydrological problems. In many cases, estimates by PTFs are simply indispensable because of the sheer cost and effort involved with direct measurements of the hydraulic characteristics. We will present a hierarchical system of PTFs based on neural network and bootstrap analyses and address several important issues. Data sets used for calibration of PTFs may contain many predictors which can be used to improve the accuracy of PTFs. However, in most hydrological studies not all required input variables may be available. To address this problem we developed a hierarchical set of five PTFs to make optimal use of limited or more extended sets of available predictors. Because all five PTFs were developed using the same data set, the predictions with the different models are consistent among each other. Besides striving for maximum accuracy and usability of PTFs, quantification of uncertainty of predicted values is also an important issue. We demonstrate that the uncertainty of PTF predictions depend not only upon the number of predictors, but also on the data that were used for calibration. The hierarchical set of PTFs is implemented in the program Rosetta (available at www.ars.usda.gov) which allows the prediction of water retention, saturated and unsaturated hydraulic conductivity. We will demonstrate the hierarchical approach using data from an IGBP initiative that provides soil hydraulic properties for the FAO soil map of the world. Finally, we will address some unresolved issues, such as the discrepancy between "structural" and "matrix" saturated hydraulic conductivities.

Am. Geophys. Union, p. 370, 1999.

A BOOTSTRAP-NEURAL NETWORK APPROACH TO PREDICT SOIL HYDRAULIC PARAMETERS

M.G. Schaap, F.J. Leij and M. Th. van Genuchten

Indirect estimation using pedotransfer PTFs of soil hydraulic properties has long received considerable attention. PTFs use regressions to predict soil hydraulic parameters from surrogate data such as soil texture and bulk density. Ideally, PTFs should provide both accurate predictions as well a measure of the reliability of those predictions. Most reviews of PTFs have focused on the accuracy, in terms of how well a particular PTF predicts hydraulic parameters of an independent data set. The reliability of PTF predictions can be quantified using the probability distribution of a prediction. Such information, normally not available, is strongly dependent upon the distribution of data in the original calibration data set. In this paper we present information about the use of a combined bootstrap-neural network procedure to predict water retention parameters, the saturated and unsaturated hydraulic conductivity, and their associated probability distributions. We also present user-friendly software that implements the developed neural-network pedotransfer functions.

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media*, Part 1, pp. 1237-1250, University of California, Riverside, CA, 1999.

COMPARISON OF PEDOTRANSFER FUNCTIONS TO COMPUTE WATER HOLDING CAPACITY USING THE VAN GENUCHTEN MODEL FOR INORGANIC SOILS

B. Imam, S. Sorooshian, T. Mayr, M.G. Schaap, H. Wosten and B. Scholes

Three different PTFs, which are used to predict parameters of the van Genuchten model, were compared using a large number of soil samples obtained from the ISRIC data set. The studied models included two regression type models developed by Wosten (the WSC mdoel) and Mayr (the SSLRC model) and one neural network model developed Schaap (USSL-NN). The comparison criterion consisted of calculating several quantitative measures of performance that are capable of addressing systematic errors, unsystematic errors, and total errors. Using observed and predicted values of the water content at several points on the theoretical pF curve, these performance measures were computed and compared for the entire sample as well as for several stratifications of the sample. The stratified study was conducted to assess the sensitivity of model performance to soil characteristics under the assumption that the robustness of each model and its applicability to a wide range of soils can be identified by assessing the sensitivity of its performance measures to soil characteristics. Throughout the comparative study, the USSL-NN model was superior both in overall performance and in sensitivity, particularly with respect to the two critical pressure levels 1/3 bar and 15 bar, both of which were selected as the default values defining water holding capacity.

Report to the IGBP-DIS soils data tasks, IGBP-DIS working paper #22. IGBP-DIS office, CNRM, Toulouse Cedex, France, 1999.

CHARACTERIZATION OF SOIL HYDRAULIC PARAMETER UNCERTAINTY

P.D. Meyer, G.W. Gee, M.L. Rockhold and M.G. Schaap

Uncertainty in predictions of contaminant transport in the environment can be significant, particularly when these predictions must be based on limited site-specific data and relatively simple models. This paper discusses the use of indirect estimation methods and large soils databases in deriving probability distributions for soil hydraulic parameters. Such distributions can be used to represent the uncertainty in model parameters. The potential effect of the type of input data used in the indirect estimation method was explored using a hierarchical neural network approach. Input to the neural networks included (1) percent sand, silt, and clay, (2) the three textural measurements plus bulk density, and (3) the textural measurements, bulk density, and water content at 33 kPa. Outputs were the parameters of the van Genuchten water retention model. Results indicate that the hydraulic parameter distributions become more representative as the amount of input data increased. The parameter distributions resulting from the neural networks were also compared to distributions from a multiple regression model. A Bayesian approach is also presented for updating soil hydraulic parameter probability distributions using site-specific data. An example illustrates the application of the method. Five site-specific estimates of the water retention parameters were used to update generic parameter probability distributions. The effect of the site-specific data on the updated net infiltration was found to be significant.

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media, Part* 2, pp. 1439-1451, University of California, Riverside, CA, 1999.

ESTIMATION OF THE SOIL HYDRAULIC PROPERTIES

M.G. Schaap, F.J. Leij and M. Th. van Genuchten

Many vadose zone studies use numerical models to simulate the movement of water and solutes in the subsurface. Knowledge about the soil hydraulic properties (for example, the water retention curve, and the saturated and unsaturated hydraulic conductivities) is essential for running most or all of these models. A broad array of methods currently exists to determine soil hydraulic properties. In the field or in the laboratory. Field methods allow for in-situ determination of the hydraulic properties but have uncertainties about the actual sample volume. Laboratory measurements require more sample preparation but do allow a larger number of measurements and a better control of the experimental conditions. Most laboratory and field techniques, however, have specific ranges of applicability with respect topsoil type and saturation. Another limitation of direct measurements is that they generally require a substantial investment in both time and money. Also, many vadose zone studies are concerned with large areas of land that may exhibit significant lateral and vertical spatial variability in the soil hydraulic properties. Performing measurements in these cases is virtually impossible, thus requiring alternative methods for estimating soil hydraulic properties. A large number of indirect methods to generate soil hydraulic properties are now also available. Although these techniques very widely in terms of methodology and complexity, all use some form of surrogate data to estimate soil hydraulic properties. In broad terms, three methods can be distinguished: pore-size distribution models, inverse methods and pedotransfer functions. This paper reviews these three types of indirect methods.

In: B. B. Looney and R. W. Falta (eds.), *Vadose Zone Science and Technology Solutions*, vol. 1, pp. 501-509, Battelle Press, Columbus, OH, 2000.

IMPROVED PREDICTION OF UNSATURATED HYDRAULIC CONDUCTIVITY WITH THE MUALEM-VAN GENUCHTEN MODEL

M.G. Schaap and F.J. Leij

In many vadose zone hydrological studies, it is imperative that the soil's unsaturated hydraulic conductivity is known. Frequently, the Mualem-van Genuchten model (MVG) is used for this purpose because it allows prediction of the unsaturated hydraulic conductivity from water retention parameters. For this and similar equations, it is often assumed that a measured saturated hydraulic conductivity (K_s) can be used as a matching point (K_0) while a factor S_e^L is used to account for pore connectivity and tortuosity (where S_e is the relative saturation and L = 0.5). We used a data set of 235 soil samples with retention and unsaturated hydraulic conductivity data to test and improve predictions with the MVG equation. The standard practice of using $K_0 = K_s$ and L = 0.5 resulted in a root mean square error for log(K) ($RMSE_K$) of 1.31. Optimization of the matching point (K_0 and L to the hydraulic conductivity data yielded a $RMSE_K$ of 0.41. The fitted K_0 were, on average, about one order of magnitude smaller than the measured K_s. Furthermore, L was predominantly negative, casting doubt that the MVG can be interpreted in a physical way. Spearman rank correlations showed that both K_0 and L were related to van Genuchten water retention parameters and neural network analyses confirmed that K_0 and L could indeed be predicted in this way. The corresponding $RMSE_K$ was 0.84, which was half an order of magnitude better than the traditional MVG model. Bulk density and textural parameters were poor predictors, while addition of K_s improved the $RMSE_K$ only marginally. Bootstrap analysis showed that the uncertainty in predicted unsaturated hydraulic conductivity was about one order of magnitude near saturation and larger at lower water contents.

Soil Sci. Soc. Am. J. 64(3):843-851, 2000.

PARAMETER CORRELATION STRUCTURES OF HYDRAULIC FUNCTIONS

M.G. Schaap and FJ. Leij

Knowledge of the statistical distribution of soil hydraulic parameters and their correlation structure is important for uncertainty analyses of water and solute transport in soils. Many studies use pedotransfer functions (PTFs) to estimate soil hydraulic properties. However, besides providing reliable predictions of hydraulic parameters, it is also important that the PTFs represent the correlation structure in the original data. We fitted various retention equations and unsaturated conductivity models to hydraulic data and examined their parameter correlations as well as those with texture and bulk density. Results for the Mualem-van Genuchten model showed that the matching point and tortuosity parameters were correlated with retention parameters, but that they exhibited only weak relations with texture. Newly developed PTFs preserve the correlation structure present in the fitted parameters and estimated unsaturated conductivity within 0.8 order of magnitude of error.

Agronomy Abstract p. 191, 1999.

EVALUATION OF EXISTING AND SITE-SPECIFIC PEDOTRANSFER FUNCTIONS TO PREDICT HYDRAULIC PROPERTIES FOR HANFORD SITE SEDIMENTS

M.G. Schaap and P.D. Meyer

The safety of current and future storage methods for radioactive waste at the Hanford waste disposal site will be assessed with conceptual models that simulate the hydrological processes in and around the disposal facilities. Presently, the appropriateness of the models is being tested using data obtained in past and recent on-site field experiments. Complicating factors are the depth of the unsaturated zone and the high degree of vertical variability in the sediments (fine sands to gravel), resulting in a high degree of spatial variability in hydraulic properties. One of the tasks is to test whether the required saturated and unsaturated hydraulic data need to be measured, or can be estimated using pedotransfer functions (PTFs). We compare the performance of an existing nation-wide PTF (Rosetta), and site-specific PTFs that were calibrated using data derived from measurements on Hanford sediments (bore holes at the 200 EW sites). An independent test was carried out for data derived from the ILAW site. The first analyses show mixed results. Predictions of water retention parameters with site-specific PTFs have generally higher correlations with independent data than predictions by the general PTF. However, when the same PTFs were evaluated on measured water contents directly, there was little difference in performance. It appears that the general PTF predicts the saturated and unsaturated conductivity much better than the site-specific PTFs. We note, however, that the currently available hydraulic data for Hanford is relatively sparse - affecting both the reliability of the site-specific PTFs and testing results. Incorporation of data from recent experiments will probably lead to better site-specific PTFs.

Am. Geophys. Union Abstracts, p. 411, 2000.

APPLICATION OF TDR AND FREQUENCY ANALYSIS TO STUDY THE CALCIC-SODIC STATUS OF A SOIL

M.G. Schaap, I. Lebron and D.L. Suarez

A change from a calcium-saturated to a sodic exchange complex often results in a marked decrease in the saturated hydraulic conductivity of soils. This reduction is probably caused by smaller pore sizes due to an increased double layer spacing resulting in the collapse of aggregates. We hypothesize that the collapse of aggregates and the formation of colloids occurs with an increase of the amount of bound water. Because bound water molecules are rotationally hindered, they have different dielectric properties than free water molecules. By determining changes in the frequency dependent dielectric spectrum, we may be able to monitor a change from a calcic to a sodic soil. We subjected a calcic soil to solutions of increasing SAR (sodium absorption ratio) and measured the saturated hydraulic conductivity as an indicator of structural collapse. We measured high-resolution TDR waveforms, which were processed with Fourier analyses to obtain scatter functions and frequency-dependent dielectric properties. Initial analyses show that instrumental difficulties sometimes make it difficult to interpret the results. Reasonable results can be obtained at low frequencies that probably show the most pronounced effects of bound water.

Agronomy Abstract p. 230, 2000.

ESTIMATES OF SOIL NITRATE DISTRIBUTIONS USING COKRIGING WITH PSEUDO-CROSSVARIOGRAMS

R. Zhang, P.J. Shouse and S.R. Yates

Nitrate (NO_3^-) is one of the major nonpoint source pollutants in the vadose zone. In this study, NO_3^- distributions were estimated in an 800 by 800 by 1.8 m soil volume using kriging and cokriging with nonsymmetric pseudo-crossvariograms. Cokriging with pseudo-crossvariograms maximized the use of available information at different soil depths. Cokriging allowed easily obtained information at shallow layers to be used to improve soil chemical estimations at deeper layers. Compared with kriging, cokriging significantly reduced the mean squared errors (MSEs) and mean kriging variances (MKVs) of the NO_3^- estimations in the soil. For the same estimation accuracy of kriging, cokriging with pseudo-crossvanograms used less than half the data; thus potentially it could reduce more than half the sampling cost than kriging estimation. Cokriging with pseudo-crossvariograms was shown to be a precise and an economic way for determining nonpoint source pollutant distributions in large fields.

J. Environ. Qual. 28:424-428, 1999.

VACUUM METHOD FOR FIELD INSTALLATION OF PIPES AND CASINGS IN SANDY SOILS

L. Ulery, S. Stewart, D.A. Reid and P.J. Shouse

Soil moisture-monitoring equipment is difficult to install in poorly consolidated sand or sediments using hand tools because the loose material tends to collapse. The technique described herein uses a 5.5-hp wet/dry vacuum cleaner, powered by a portable gasoline generator, to remove the soil while an operator pushes a conductor pipe or casing into the profile. After initiating the hole using a hand bucket auger, an open-ended metal pipe or polyvinyl chloride (PVC) casing is inserted vertically into the shallow hole. A smaller tube, or stinger, attached to a wet/dry vacuum is inserted into the pipe to extract loose material while downward pressure is applied on the pipe. Once the casing is installed, instrumentation such as lysimeters, gypsum blocks, or tensiometers can be placed at the desired depth and backfilled with native soil. The casing is then raised and the soil allowed to collapse around the equipment, or the pipe can be left in place for neutron probe access. Measurements of soil water content after an infiltration experiment demonstrated uniform downward movement with minimal preferential flow or soil disturbance as a result of the vacuum installation of gypsum blocks and a neutron access tube.

Soil Sci.165:269-273, 2000.

SPATIAL DEPENDENCE OF SOIL WATER RETENTION AND THERMAL PROPERTIES OF A SANDY LOAM SOIL

P.J. Shouse , B.P. Mohanty and T.H. Skaggs

Energy exchanges at the soil surface are propagated into the soil profile by a complex series of transport processes with rates affected by soil properties varying in both space and time. Our project focuses on the variation of volumetric heat capacity, thermal conductivity, and thermal diffusivity as functions of space and soil water retention. We measured the thermal properties of a sandy loam soil using the dual heat probe method on undisturbed soil cores equilibrated to different soil water pressure heads. The measured thermal properties depend on the water content and to a lesser extent the bulk density. Both thermal and retention properties varied in space as well.

Agronomy Abstract p. 193, 1999.

NONLINEAR DYNAMICS OF SOIL MOISTURE AND TEMPERATURE AT DIFFERENT SCALES

P.J. Shouse, T.H. Skaggs and B.P. Mohanty

Dynamics of soil moisture and temperature at different spatio-temporal scales is critical for land-atmosphere interaction. We used gridded ground-based impedance probe water content data and aircraft-mounted Electronically Scanned Thinned Array Radiometer (ESTAR) pixel-average soil moisture data to investigate the spatio-temporal evolution and time-stable characteristics of soil moisture in three selected footprints from the Southern Great Plains 1997 (SGP97) Hydrology Experiment in Oklahoma. Better time stable features were observed within a footprint containing sandy loam soil than within two pixels containing silty loam soil. Additionally, flat topography with split wheat/grass land cover produced the largest spatio-temporal variability and the least time stability in soil moisture patterns. A comparison of ground-based and remote sensing data showed that ESTAR footprint-average soil moisture was well calibrated for the pixel with sandy loam soil, rolling topography, and pasture land cover, but improved calibration is warranted for the silty loam soil, rolling topography, pasture land and silty loam soil, flat topography, split vegetation of wheat and grass land with tillage practice pixels. Results from another field-scale soil moisture and temperature dynamics experiment in a sandy loam soil, flat topography, bare land cover, and semi-arid climate of Riverside, California will also be presented.

Agronomy Abstract p. 218, 2000.

APPLICATION OF MOMENT ANALYSIS FOR ESTIMATING TRANSPORT AND REACTION PARAMETERS FROM BREAKTHROUGH CURVES

B.S. Das, I.W. Wraith, H.W. Langner, P.J. Shouse and G.J. Kluitenberg

The method of moments (MOM) was critically examined for estimating solute transport parameters and analyzing transport processes. Parameters were estimated from both laboratory- and field-measured breakthrough curves using the MOM and the conventional least-squares method. Results show that these two procedures yield similar estimates when a complete mass recovery is obtained. In cases of incomplete mass recovery, parameters associated with higher-order moments depart significantly from those estimated using least-squares methods. This suggests that where the MOM is indispensable, a complete mass balance should be ensured during the experimentation. Results of process analysis show that nonequilibrium indices, defined with moments, reveal interactions among transport and reaction processes. However, it is not possible to quantify these interactions unless extreme bounds for the indices are properly defined.

Agronomy Abstract p. 219, 2000.

INVERSE OPTIMIZATION, CALIBRATION AND VALIDATION OF SIMULATION MODELS AT THE FIELD SCALE

J. Šimůnek and J.A. de Vos

An overview is given of the issues of parameter estimation, model verification, and model validation as applied to field-scale subsurface flow and transport problems. We briefly review inverse optimization methods for estimating soil hydraulic parameters from a variety of field experiments, including tension disc infiltrometry, cone penetrometry, and gravity drainage experiments. An example is presented showing calibration of the numerical HYDRUS-2D model using data of a tile-drainage experiment. The hydraulic characteristics of the layered soil profile at the site were identified based on the joined use of laboratory data, field monitoring data, and the numerical model. A split sampling technique was used to test applicability of the numerical model for this study.

In: J. Feyen and K. Wiyo (eds.), *Modelling of Transport Process in Soils at Various Scales in Time and Space*, pp. 431-445, Wageningen Pers, Wageningen, The Netherlands, 1999.

HORIZONTAL INFILTRATION REVISITED USING PARAMETER ESTIMATION

J. Šimůnek, J.W. Hopmans, D.R. Nielsen and M. Th. van Genuchten

A parameter estimation approach (the HYDRUS-1D model) was used to analyze horizontal infiltration data for Columbia silt loam and Hesperia sandy loam, presented and investigated previously by Nielsen et al. (1962) using the analytical method of Bruce and Klute (1956). Similarly to the original analysis, water content profiles at the different times could be accurately optimized in a simultaneous fashion only when the applied pressure head was close to saturation (-2 cm). For much lower boundary pressures (-50 and -100 cm), water content profiles for the different times had to be optimized independently. Excellent agreement was obtained between diffusivities calculated either analytically or numerically from the same water content profiles. In addition to diffusivities, the numerical parameter estimation analysis of the horizontal infiltration experiments provided estimates of the soil-water retention and hydraulic conductivity functions.

Am. Geophys. Union, p. 363, 1999.

ESTIMATING HYSTERESIS IN THE SOIL WATER RETENTION FUNCTION FROM CONE PERMEAMETER EXPERIMENTS

J. Šimůnek, R. Kodesova, M.M. Gribb and M. Th. van Genuchten

Data obtained from modified cone penetrometer experiments were used to estimate the hysteretic soil hydraulic properties with a parameter estimation technique which combined a numerical -solution of the Richards equation with Marquardt-Levenberg optimization. The modified cone penetrometer was designed to inject water into a soil through a cylindrical screen, measure the infiltration rate with time, and track the movement of the wetting front using two tensiometer rings positioned above the screen. After reaching relatively stable tensiometer readings during the experiments, the source of water was cut off and pressure head readings measured while water in the soil profile redistributed. Cumulative inflow and pressure head readings for two experiments with different supply pressures were analyzed to obtain estimates of the soil water retention and hydraulic conductivity functions. Analysis of flow responses obtained during the infiltration period, and of those obtained during the combined infiltration and redistribution phases, demonstrated the importance of hysteresis of the soil hydraulic functions. We found that the redistribution phase could not be described accurately when hysteresis was neglected. Hysteresis in the soil hydraulic functions was modeled using a relatively simple empirical model in which wetting scanning curves are scaled from the main wetting curve and drying scanning curves are scaled from the main drying curve. This model was deemed adequate for our examples. Optimization results for various combinations of unknown soil hydraulic parameters were compared to results of standard laboratory and in situ methods. Estimates of the saturated hydraulic conductivity were well within the range of in situ measurements. The estimated main hysteretic loops of the soil water retention curve were for the most part situated between the wetting and drying curves obtained with standard methods.

Water Resour. Res. 35(5):1329-1345, 1999.

USING THE HYDRUS-1D AND HYDRUS-2D CODES FOR ESTIMATING UNSATURATED SOIL SOLUTE TRANSPORT PARAMETERS

J. Šimůnek, M. Th. van Genuchten and M. Sejna

In this paper we describe a parameter estimation procedure which combines the Levenberg-Marquardt nonlinear parameter optimization method involving weighted least squares with either a one-dimensional numerical model (HYDRUS-1D) or a two- or quasi three-dimensional model (HYDRUS-2D), which solve the governing equations for water flow and solute transport in variably-saturated porous media. The procedure permits several unknown parameters in the unsaturated soil-hydraulic functions to be estimated from observed water contents, pressure heads, and/or instantaneous or cumulative boundary fluxes (e.g., infiltration or outflow data) during transient water flow by numerical inversion of the Richards equation. Additional retention or hydraulic conductivity data, as well as a penalty function for constraining the optimized parameters to remain in some feasible region (Bayesian estimation) can be optionally included in the parameter estimation procedure. Similarly, the procedure permits solute transport and/or reaction parameters to be estimated from observed concentrations and/or instantaneous or cumulative boundary solute fluxes during transient solute transport by numerical inversion of the convection-dispersion equation. The unsaturated soil hydraulic and solute transport and reaction parameters can be estimated either sequentially or simultaneously. Depending upon the quality of observed data, soil hydraulic or solute transport parameters for several soil layers can be estimated simultaneously. The parameter estimation procedure is demonstrated for several laboratory and field experiments.

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media*, Part 1, pp. 1523-1536, University of California, Riverside, CA, 1999.

THE HYDRUS-2D SOFTWARE PACKAGE FOR SIMULATING TWO-DIMENSIONAL MOVEMENT OF WATER, HEAT, AND MULTIPLE SOLUTES IN VARIABLY--SATURATED MEDIA, VERSION 2.0

J. Šimůnek, M. Sejna and M. Th. van Genuchten

This report documents version 2.0 of HYDRUS-2D, a software package for simulating water, heat, and solute movement in two-dimensional variably saturated media. The software package consists of the HYDRUS2 computer program, and the interactive graphics-based user interface HYDRUS2D. The HYDRUS-2D program numerically solves the Richards' equation for saturated-unsaturated water flow and the convection-dispersion equation for heat and solute transport. The flow equation incorporates a sink term to account for water uptake by plant roots. The heat transport equation considers transport due to conduction and convection with flowing water. The solute transport equations consider convective-dispersive transport in the liquid phase, as well as diffusion in the gaseous phase. The transport equations also include provisions for nonlinear nonequilibrium reactions between the solid and liquid phases, linear equilibrium reactions between the liquid and gaseous phases, zero-order production, and two first-order degradation reactions: one which is independent of other solutes, and one which provides the coupling between solutes involved in sequential first-order decay reactions. In addition, physical nonequilibrium solute transport can be accounted for by assuming a two-region, dual-porosity type formulation which partitions the liquid phase into mobile and immobile regions. This version 2.0 of HYDRUS-2D also includes a Marquardt-Levenberg type parameter optimization algorithm for inverse estimation of soil hydraulic and/or solute transport and reaction parameters from measured transient or steady-state flow and/or transport data.

The program is distributed by means of two different options. Option A pertains to the executable HYDRUS2 code (a modification of the former CHAIN-2D code) for use with a graphics-based user interface, HYDRUS2D, for easy data preparation and output display in the MS Windows environment. This option also includes the HYDRUS2D interface, and a structured mesh generator for relatively simple flow domain geometries. Option B additionally includes a CAD program for more general domain geometries, and the MESHGEN2D mesh generator for an unstructured finite element mesh specifically designed for variably-saturated subsurface flow transport problems. This report serves as both a user manual and reference document. Detailed instructions are given for data input preparation.

IGWMC-7PS-53, Int. Ground Water Modeling Center, Colorado School of Mines Golden, CO. 251 p., 1999.

INVERSE ANALYSIS OF TRANSIENT VARIABLY-SATURATED WATER FLOW AND SOLUTE TRANSPORT COLUMN STUDIES

J. Šimůnek, J. Vanderborght and M. Th. van Genuchten

Two transient water flow and solute transport column experiments were studied using an inverse analysis. Large undisturbed soil columns (0.3-m i.d., 1-m long, 4 major soil horizons) were subjected to a periodic upper boundary con(involving a constant flow rate followed by a no-flow condition, with a period of 1 day. The lower boundary condition was either a constant pressure head I cm below a ceramic plate) or a seepage face (no ceramic plate). The soil was characterized as a sandy loam with a highly degraded illuvial day hot Water contents and solute concentrations were measured at 13 locations horizontally installed TDR probes. We first calibrated the water flow model against the water content measurements. The measured information was not deemed sufficient to estimate the true soil hydraulic parameters. Because resistances against water flow caused by the low-conductivity ceramic I great difficulties were encountered in calibrating the flow model using data for the constant lower boundary condition. Calibrated water flow fields measured concentrations were subsequently used to estimate dispersivities of particular soil horizons. Breakthrough curves at particular locations analyzed both sequentially and simultaneously. Results of the inverse analysis were compared with results of a quasi steady-state solution.

Geophysical Research Abstracts, European Geophysical Society 1(2):311, 1999.

ESTIMATING UNSATURATED SOIL HYDRAULIC PROPERTIES FROM LABORATORY TENSION DISC INFILTROMETER EXPERIMENTS

J. Šimůnek, O. Wendroth and M. Th. van Genuchten

Four tension disc infiltration experiments were carried out on a loamy soil in the laboratory for the purpose of estimating the unsaturated soil hydraulic properties. Sixteen tensiometers were installed in pairs at the following coordinate (r, z) positions: (10, 2.5), (10, 5), (10, 10), (15, 5), (15, 10), (15, 15), (15, 20), and (15, 30), where y represents the distance from the axis of symmetry and z is the location below the soil surface. A time domain reflectometry (TDR) probe was used to measure water contents at a depth of 2 cm directly below the tension disc. The first three experiments involved supply pressure heads at the disc of -20, -10, -;5, and -1 cm, with the experiment lasting for approximately 5 hours. The same supply pressure heads were also used for the fourth experiment, which lasted 6.25 days so as to reach steady state at each applied tension. The measured data were analyzed using Wooding's [1968] analytical solution and by numerical inversion. The parameter estimation method combined a quasi three-dimensional numerical solution of the Richards equation with the Marquardt-Levenberg optimization scheme. The objective function for the parameter estimation analysis was defined using different combinations of the cumulative infiltrated volume, TDR readings, and tensiometer measurements. The estimated hydraulic properties were compared against results obtained with an evaporation experiment as analyzed with Wind's [1968] method. Water contents in the retention curves were underestimated when both transient and quasi steady-state experiments were analyzed by parameter estimation. Unsaturated hydraulic conductivities obtained by parameter estimation and using Wooding's [1968] analysis corresponded well. Drying branches of the hydraulic conductivity function determined by parameter estimation also corresponded well with those obtained with the evaporation method.

Water Resour. Res. 35(10):2965-2979, 1999.

SOIL HYDRAULIC PROPERTIES FROM LABORATORY EVAPORATION EXPERIMENTS BY PARAMETER ESTIMATION

J. Šimůnek, O. Wendroth and M. Th. van Genuchten

We estimated the soil hydraulic properties from laboratory evaporation experiments using a parameter estimation method and the modified method of *Wind* [1968]. We used both numerically generated data and data measured in the laboratory. Two experiments with two different soils were performed in the laboratory. Both numerical and laboratory experiments were carried out on 10-cm high soil cores. Pressure heads inside the cores were measured with tensiometers at five different depths. While evaporative water loss from the top was determined by weighing the soil samples in the laboratory, a constant evaporation rate was specified for numerical experiments. The objective function for the parameter estimation analysis was defined in terms of the final total water volume in the core and pressure head readings of one or several tensiometers. An analysis of numerically generated data showed that the optimization method was most sensitive to the hydraulic parameters n and θ_s and least to θ_r (θ_s is the saturated water content, θ_r is the residual water content, and n is a hydraulic property shape factor). Numerical analysis also showed a very high correlation between parameters θ_r and n. Pressure heads measured close to the soil surface were found to be more valuable for the parameter estimation technique than those measured at greater depths. The optimized hydraulic parameters for the laboratory soil samples corresponded closely with those obtained using Wind's analysis. All optimizations gave similar results for the soil hydraulic properties within the measurement range of the soil water pressure head (0 to -700 cm). Extrapolation beyond this range yielded a high level of uncertainty.

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media*, Part 1, pp. 713-724, University of California, Riverside, CA, 1999.

ESTIMATING HYSTERESIS IN THE SOIL WATER RETENTION FUNCTION FROM A COMBINED UPWARD INFILTRATION AND EVAPORATION EXPERIMENT

J. Šimůnek, O. Wendroth, N. Wypler and M. Th. van Genuchten

Data obtained from an upward infiltration experiment followed by evaporation were used to estimate the hysteretic soil hydraulic properties. The invoked parameter estimation technique combined a numerical solution (HYDRUS- 1 D) of the Richards equation with Marquardt-Levenberg optimization. The laboratory experiments were carried out on 10-cm long soil cores having an internal diameter of 10 cm. A constant pressure head of 10 cm was used as the lower boundary condition for the upward infiltration experiment. A two-rate evaporation approach was followed for the evaporation experiment. Pressure heads inside the cores were measured with five tensiometers while evaporative water loss from the top was determined by weighing the soil samples. The objective function for the parameter estimation analysis was defined in terms of pressure head readings and the cumulative infiltration rate during upward infiltration and the final total water volume in the core as well as pressure head readings during the evaporation part. Analysis of flow responses obtained during the combined infiltration and evaporation phases demonstrated the importance of hysteresis of the soil hydraulic functions. We found that the evaporation phase could not be described accurately when hysteresis was neglected. The optimized hydraulic parameters were compared against those obtained using Wind's analysis.

Geophysical Research Abstracts, 1(2), European Geophysical Society: 305, 1999.

REVIEW OF INVERSE ESTIMATION OF SOIL HYDRAULIC PROPERTIES

J.W. Hopmans and J. Šimůnek

Parameter estimation of flow and transport properties using numerical modeling of transient flow and transport experiments in combination with an optimization code has been applied only to a limited extend, principally for the estimation of soil hydraulic functions. The parameter estimation method is attractive since it applies to transient experiments and is therefore not constraint to assumptions of analytical solutions. Experiments could be designed to be simple and short, relative to methods that require static or near-equilibrium conditions. Although the inverse technique has been successfully applied by many, others have hesitated to investigate this method, because of lack of information or guidelines with regard to experimental setup, type, error and frequency of measurements, choice of optimization code, and unfamiliarity with technical jargon. Consequently, parameter estimation using transient experiments has been studied only to a limited extend. In many cases, questions arise with regard to which parameters to optimize, to the influence of errors associated with the optimized parameters, and which flow or transport variables to be included in the minimization function. A review of the inverse estimation of soil hydraulic characteristics will be presented.

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop*, Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media, Part* 1, pp. 643-660, University of California, Riverside, CA, 1999.

USING A MULTI-STEP SOIL -WATER EXTRACTION TECHNIQUE FOR IN-SITU ESTIMATION OF SOIL HYDRAULIC PROPERTIES

M. Inoue, J. Šimůnek , J.W. Hopmans and V. Clausnitzer

Estimation of soil hydraulic properties is important to effectively provide input for transient water flow and solute transport simulations and predictions. The objective of this study was to demonstrate the potential application of in-situ soil water extraction to estimate soil water retention and unsaturated hydraulic conductivity parameters. The Levenberg-Marquardt algorithm in combination with the HYDRUS-2D flow code was used to inversely estimate the parameters of the hydraulic functions from transient soil matric potential and cumulative soil solution extraction measurements. An experiment was carried out in a field soil consisting of Yolo silt loam. A series of vacuum extraction pressures was applied to a ceramic soil solution sampler, and cumulative soil solution extraction volumes and matric potential heads at various locations near the extraction device were monitored during extraction. A power function determined from measured tensiometric data was used to calculate the matric potential at the lower boundary. The upper boundary was defined as a zero flux boundary. Cumulative extraction volume and matric potential data were included in an objective function that was minimized to estimate the parameters describing the hydraulic functions. We determined that the inverse solution was sensitive to the hydraulic resistance of the ceramic cylinder of the extraction device. The optimized parameters were correctly estimated after we included in the objective function three independently measured soil water retention data points determined during the extraction experiment. Comparison of the optimized soil hydraulic parameters with those determined independently with the instantaneous profile method indicated that the in-situ estimation using a multi-step soil-water extraction technique can provide accurate soil hydraulic data.

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media, Part* 1, pp. 725-736, University of California, Riverside, CA, 1999.

ESTIMATION OF SOIL HYDRAULIC AND SOLUTE TRANSPORT PARAMETERS FROM TRANSIENT COLUMN EXPERIMENTS

M. Inoue, J. Šimůnek , S. Shiozawa and J.W. Hopmans

Estimation of soil hydraulic and solute transport parameters is important to provide input parameters for numerical models simulating transient water flow and solute transport. The Levenberg-Marquardt algorithm in combination with the HYDRUS-1 D (version 2.0) code was used to inversely estimate several unsaturated soil hydraulic and solute transport -parameters from transient pressure head, volumetric water content, and solute (NaCl) concentration measurements. A 30-cm long coarse-textured soil column having an internal diameter of 5 cm was used for the infiltration experiments. Experiments were carried out with both increasing and decreasing solute concentrations following sudden increases in the infiltration rate for the sand column. Pressure heads, volumetric water contents, and solute concentrations were measured using electric mini-tensiometers and four-electrode sensors. The optimization results were compared with independently measured soil water retention, unsaturated hydraulic conductivity, and solute dispersion data. The optimized values corresponded well with those measured independently within the range of experimental data.

Geophysical Research 1(2), European Geophysical Society, 311, 1999.

NUMERICAL SIMULATION OF TRANSPORT AND SEQUENTIAL BIODEGRADATION OF CHLORINATED ALIPHATIC HYDROCARBONS USING CHAIN-2D

D. Schaerlaekens, D. Mallants, J. Šimůnek and M. Th. van Genuchten

Microbiological degradation of perchloroethylene (PCE) under anaerobic conditions follows a series of chain reactions, in which, sequentially, trichloroethylene (TCE), cis-dichloroethylene (c-DCE), vinylchloride (VC) and ethene are generated. First-order degradation rate constants, partitioning coefficients and mass exchange rates for PCE, TCE, c-DCE and VC were compiled from the literature. The parameters were used in a case study of pump-and-treat remediation of a PCE-contaminated site near Tilburg, The Netherlands. Transport, non-equilibrium sorption and biodegradation chain processes at the site were simulated using the CHAIN-2D code without further calibration. The modelled PCE compared reasonably well with observed PCE concentrations in the pumped water. We also performed a scenario analysis by applying several increased reductive dechlorination rates, reflecting different degradation conditions (e.g., addition of yeast extract and citrate). The scenario analysis predicted considerably higher concentrations of the degradation products as a result of enhanced reductive dechlorination of PCE. The predicted levels of the very toxic compound VC were now an order of magnitude above the maximum permissible concentration levels.

Hydrol. Process 13:2847-2859, 1999.

IDENTIFICATION OF THE HYDRAULIC CHARACTERISTICS OF A LAYERED SILT LOAM

J.A. de Vos, J. Šimůnek, P.A.C. Raats and R.A. Feddes

The hydraulic characteristics of a layered silt loam were identified, based on the joint use of laboratory data, field monitoring data, and the two-dimensional Hydrus-2D model. Laboratory water retention and hydraulic conductivity characteristics and hydraulic conductivities at saturation were used in the Hydrus-2D model, with successive infiltration rates of 0.5, 1, 2, 3, 6, 10, 15, 20 and 25 mm d^{-1}. The hydraulic conductivities at saturation for the different layers were optimised by comparing simulated (steady) and observed drain discharge rate - groundwater level relationships. Further adjustments were made on the basis of field-measured water retention characteristics for the 0-25 cm topsoil. It is shown that the hydraulic properties, in combination with a drain tile spacing of 12 m and typical weather patterns, lead to highly variable flow patterns. These varying flow patterns and momentary spatial distributions of the solutes explain the typical fluctuations of the solute concentration in the drainage water in relation to fluctuations in the drain discharge rate.

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media, Part* 1, pp. 783-798, University of California, Riverside, CA. 1999.

SOIL HYDRAULIC PROPERTIES DETERMINED FROM EVAPORATION AND TENSION INFILTRATION EXPERIMENTS AND THEIR USE FOR MODELING FIELD MOISTURE STATUS

O. Wendroth and J. Šimůnek

Accurate determination of soil hydraulic properties over a wide range of moisture contents, especially close to water saturation still provides some difficulties. Moreover, the suitability of hydraulic properties determined under laboratory conditions for modeling field soil water status has to be proven. This study focuses on the correspondence between a modified Wind method and a steady-state disk permeameter infiltration method. Hydraulic properties determined in the laboratory were used for simulation of field soil water content time series, and the effect of a stochastic filter (Kalman Filter) on the prediction of soil water content with a state-space approach was evaluated. Results from both laboratory methods corresponded well. With a realistic estimate of field soil evaporation, lab-determined properties were suitable for simulation of field soil moisture status. While observations are taken into account in the state-space prediction, uncertainties due to e.g. an unrealistic high estimate of evaporation could be compensated.

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media*, Part 1, pp. 737-748, University of California, Riverside, CA, 1999.

THE DISC COMPUTER SOFTWARE FOR ANALYZING TENSION DISC INFILTROMETER DATA BY PARAMETER ESTIMATION, VERSION 1.0

J. Šimůnek and M. Th. van Genuchten

This report documents version 1.0 of DISC, a computer software package for analyzing tension disc infiltrometer data by parameter estimation. The software package consists of the simplified HYDRUS2 computer program, and an interactive graphics-based user interface. The DISC code numerically solves the Richards' equation for saturated-unsaturated water flow. Flow occurs in a three-dimensional region exhibiting radial symmetry about the vertical axis. The software includes a Marquardt-Levenberg type parameter optimization algorithm for inverse estimation of soil hydraulic from measured transient cumulative infiltration and related data.

The governing flow and transport equations are solved numerically using Galerkin-type linear finite element schemes. The transport region is discretized automatically by the software into triangular elements using pregenerated files that are scaled directly to the specified size of the tension disc radius.

This report serves as both a user manual and reference document. Detailed instructions are given for data input preparation.

Research Report No. 145, U.S. Salinity Laboratory, USDA, ARS, Riverside CA. 34 p, 2000.

INVERSE ESTIMATION OF UNSATURATED SOIL HYDRAULIC AND SOLUTE TRANSPORT PARAMETERS USING THE HYDRUS-1D CODE

J. Šimůnek and M. Th. van Genuchten

A numerical code (HYDRUS-1D) was developed for identifying soil-hydraulic and solute transport parameters from unsaturated flow and transport data in a on dimensional porous media. The utility of the code was demonstrated using data typically obtained during multistep outflow experiment, horizontal infiltration followed by redistribution, and a column miscible displacement (breakthrough) study. Because of its generality (in terms of the definition of the objective function, the possible combination of different boundary and initial conditions, and options for considering multi-layered systems), HYDRUS-1D is an extremely useful tool for analyzing a broad range of steady-state and transient laboratory and in-situ field flow and transport experiments.

In: Brian B. Looney and Ronald W. Falta (eds.), *Vadose Zone Science and Technology Solutions*, vol. 2, pp. 815-827, Battelle Press, Columbus, OH, 2000.

RETCML: INCORPORATING MAXIMUM-LIKELIHOOD ESTIMATION PRINCIPLES IN THE RETC SOIL HYDRAULIC PARAMETER ESTIMATION CODE

K.J. Hollenbeck, J. Šimůnek and M. Th. van Genuchten

RETC is a public domain computer code for estimating parameters of the water retention curve and hydraulic conductivity functions of unsaturated soils. RETC was developed at the U. S. Salinity Laboratory and is now used world-wide with thousands of copies distributed. Evaluation of the final estimation results in the code has been improved to yield a new version, RETCML, based on maximum-likelihood theory for the special case of weighted least-squares estimators. This paper first explains the theory of maximum-likelihood and introduces the principles of model adequacy and parameter uncertainty on a formal basis. Next, this paper presents a user guide for the code. RETCML is also free and has been programmed to be almost fully compatible with the original RETC input files, thus making it easy to re-analyze previous data. The output of RETCML includes a thorough evaluation of estimation results.

Computer & Geosciences 26(3):319-327, 2000.

INFILTRATION OF WATER INTO SOIL WITH CRACKS

V. Novak, J. Šimůnek and M. Th. van Genuchten

This paper presents the physical basis of the FRACTURE submodel for simulating infiltration of precipitation/irrigation water into relatively dry, cracked, fine-textured soils. The FRACTURE submodel forms part of the HYDRUS-ET variably saturated flow/transport model. Infiltration into the soil matrix is formally divided into two components: (1) vertical infiltration through the soil surface; and (2) lateral infiltration via soil cracks. The first component is described and solved using the 1D Richards' equation. Excess water that does not infiltrate through the soil surface is either considered to be runoff if no soil cracks are present, or routed into soil cracks from where it may laterally infiltrate into the soil matrix. Horizontal infiltration from soil cracks into the soil matrix is calculated using the Green-Ampt approach and incorporated as a positive source/sink term in the Richards' equation describing flow in the matrix. In addition to the hydraulic properties of the soil matrix, the FRACTURE submodel requires parameters characterizing the soil cracks, notably the specific crack length per surface area, and the relationship between crack porosity, and the gravimetric soil water content. An example problem shows that infiltration from soil cracks can be an important process affecting the soil water regime of cracked soils. A comparison with the more traditional approach involving surface infiltration only, indicates important differences in the soil water content distribution during a rainfall/irrigation event. This extension of the classical approach to include crack infiltration significantly improves the identification and prediction of the soil water regime.

J. Irrig. & Drain. Engrg. 126(1):41-47, 2000.

NONEQUILIBRIUM WATER FLOW CHARACTERIZED FROM AN UPWARD INFILTRATION EXPERIMENT

J. Šimůnek, O. Wendroth, N. Wypler and M.Th. van Genuchten

Data obtained from upward tension infiltration experiments were analyzed using the single-porosity Richards equation, as well as variably-saturated dual porosity and dual-permeability models characterizing nonequilibrium water flow. The laboratory experiments were carried out on 10-cm long soil cores having an internal diameter of 10 cm. Constant pressure heads of -10 and -1 cm were used as the lower boundary condition for the upward infiltration experiment. Each infiltration was followed by a one-rate evaporation experiment to reestablish initial conditions and to obtain the drying soil hydraulic properties. Pressure heads inside the cores were measured using five tensiometers, while evaporative water loss from the top was determined by weighing the soil samples. The data were analyzed using a parameter estimation technique that combined a numerical solution (the modified HYDRUS-1D) of the governing flow equation with Marquardt-Levenberg optimization. Analysis of flow responses obtained during the infiltration experiment demonstrated significant nonequilibrium flow behavior. This behavior could be well characterized using a two-region physical nonequilibrium model that divides the medium into inter- and intra-aggregate pores with first-order transfer of water between the two systems.

Geophysical Research Abstracts, European Geophysical Society p. 215, 2000.

THE HYDRUS-1D AND HYDRUS-2D CODES FOR ESTIMATING UNSATURATED SOIL HYDRAULIC AND SOLUTE TRANSPORT PARAMETERS

J. Šimůnek, M. Sejna and M. Th. van Genuchten

We present new versions of the HYDRUS- 1 D and -2D software packages and demonstrate their use for estimating soil hydraulic and solute transport parameters. Both models can be calibrated for water flow and solute transport in single- or multi-layered systems. Pressure head, water content,and/or concentrations at several locations, fluxes across boundaries, and independently measured retention and/or hydraulic conductivity data, can be include in the objective function. We present applications of HYDRUS-1D for estimating soil hydraulic and transport parameters from one- and multi-step outflow experiments, evaporation experiments, upward infiltration, horizontal infiltration followed by redistribution, and column breakthrough curves. Applications of HYDRUS-2D are presented for data obtained using a multistep soil-water extraction technique, a modified cone penetrometer, and a tension disc infiltrometer.

Agronomy Abstract p. 357, 1999.

THE STANMOD COMPUTER SOFTWARE FOR EVALUATING SOLUTE TRANSPORT IN POROUS MEDIA USING ANALYTICAL SOLUTIONS OF THE CONVECTION-DISPERSION EQUATION

J. Šimůnek, M. Th. van Genuchten, M. Sejna, N. Toride and F.J. Leij

A large number of computer programs now exists for evaluating solute transport in porous media using analytical solutions of the convection-dispersion equation. The purpose of this project was to integrate the most widely used models into one software package. STANMOD (STudio of ANalytical MODels) is a Windows based computer software package for evaluating solute transport in porous media using analytical solutions of the convection-dispersion solute transport equation. STANMOD includes the following models for one-dimensional transport problems: CXTFIT 2.0 (Toride et al., 1995), CFITM (van Genuchten, 1980), CFITIM (van Genuchten, 1981), and CHAIN (van Genuchten, 1985). STANMOD also includes the models 3DADE (Leij and Bradford, 1994) and N3DADE (Leij and Toride, 1997) for two- and three- dimensional transport problems. The graphics-based user-interface of STANMOD is largely based on libraries developed for the HYDRUS- 1D and HYDRUS-2D) software packages. We present several illustrative examples of breakthrough curve analyses.

Agronomy Abstract p. 418, 2000.

LOCALIZED GROUND WATER RECHARGE THROUGH PIPES IN CALCIC HORIZONS

G. Rodriguez-Marin, J. Šimůnek, I.B. Harrison and J.M. Hendrickx

Small and large pipes have been observed in many indurated calcic horizons in New Mexico. A survey on the La Mesa surface in southern New Mexico along a 30 km long trench revealed that the area occupied by pipes varied from 15 to 19 percent. Therefore, we hypothesize that pipes play an important role for localized ground water recharge. We will present field measurements and simulations with the model HYDRUS-2D) to test this hypothesis.

Agronomy Abstract p. 217, 2000.

CRITICAL PATH ANALYSIS OF PORE-SCALE NETWORK MODELS: POWER LAW LOCAL CONDUCTIVITIES AND FINITE-SIZED SYSTEMS

T.H. Skaggs and A.G. Hunt

Network models of randomly sized capillary tubes are commonly used as surrogate media in theoretical investigations of the transport properties of soils and rocks. The conductivity of network models can be calculated by critical path analysis (CPA), a method based on the connectivity of highly conducting pathways and the statistics of percolation theory. It is well established that CPA accurately calculates the steady-state conductivity of infinitely sized networks when: (1) local conductivities are spatially uncorrelated, (2) local conductivities are broadly distributed (spanning at least four orders-of-magnitude), and (3) local conductivities are exponential functions of random variables (e.g. capillary tube radii). Recently, Hunt (1998) used cluster statistics to show that the CPA conductivity can be corrected for finite-sized systems, and derived a probabilistic relationship in which the expected system conductivity decreases with increasing system size (this result requires that the local conductivity distribution be independent of system size). We will show that there are subtleties involved in the application of CPA when the local conductivity is a power law function of random variables rather than an exponential function, as is the case when local flow is according to Poiseuille's Law. When there is a power law dependence, the distance between critical bonds diminishes to point where percolation statistic no longer apply, and conductance occurs on non-tortuous pathways that are nothing like those obtained for an exponential dependence. Additionally, we will show that the conductivity can be an increasing function of system size when the local conductivity distribution has a system-size dependent maximum. The analytical CPA results will be compared with numerical network calculations.

Am. Geophys. Union, p. 441, 1999.

PREDICTING SOIL PARTICLE-SIZE DISTRIBUTIONS FROM TEXTURE DATA

T.H. Skaggs, P.J. Shouse, L.M. Arya and B.P. Mohanty

Previously, methods have been developed for predicting the soil-water retention curve from the more easily measured particle-size distribution (PSD). Often, however, it is necessary to estimate retention properties when only soil texture data are available (percent sand, silt, and clay), rather than the full PSD. We conducted a study to determine if it is possible to predict the PSD from soil texture data. Procedures were developed for relating texture data to parameter values in several candidate models of the PSD. The estimation methods were tested on approximately 100 soils from the SGP97 and UNSODA databases. The results were mixed, with some of the predicted PSDs being very accurate, while others were somewhat poor. Ongoing efforts are aimed at refining the methods and identifying the conditions under which accurate predictions can be expected.

Agronomy Abstract p. 191, 1999.

A PROBABILISTIC RELATIONSHIP BETWEEN THE HYDRAULIC AND ELECTRICAL CONDUCTIVITIES AS A FUNCTION OF SCALE

G. Hunt and T.H. Skaggs

Recent work using critical path analysis has indicated a simple relationship between the hydraulic, g^h, and electrical, g^e, conductivities of heterogeneous porous media. In that work, ionic concentration was treated as being uniform and the application of critical path analysis required the system size be infinite. We consider the effects of variability in ionic concentration and finite-size scaling, and use cluster statistics of percolation theory to determine a probabilistic relationship between g^e and g^h. We also clarify some aspects of the application of percolation theory and critical path analysis to saturated soils when local conductances are power laws of the radii of connecting pores. Conduction is shown to take place along paths that are not tortuous (in the sense of percolation theory).

Agronomy Abstract p. 191, 1999.

SOIL WATER AND SALINITY USING TDR DURING CYCLIC WETTING AND DRYING

T.H. Skaggs, P.J. Shouse and P. Castiglione

Time-domain reflectometry (TDR) is a potentially useful tool for monitoring water content and soil salinity in the irrigated west. Calibrating the TDR for meaningful salinity measurements can be difficult. We set up several experiments to help us determine the proper calibration for conditions of non-steady non-uniform water contents; one using cyclic irrigation and evaporation, and one using drainage from saturation with no evaporation. Our results indicate that a linear calibration model may be more appropriate for calculating the electrical conductivity of soil water (ECsw) or the electrical conductivity of the saturated soil paste extract (ECe). Further experiments are planned and results will be reported.

Agronomy Abstract p. 27, 2000.

SOIL PHYSICAL PROCESSES FROM THE PORE TO THE PEDON

M. Th. van Genuchten

The past several decades has seen tremendous progress in the conceptual understanding and mathematical description of vadose zone flow and transport processes. A large number of analytical and numerical models of varying degrees of complexity and dimensionality are now available to predict water flow and solute transport in variably-saturated porous media. The purpose of this presentation was to highlight recent progress in flow/transport research at especially the local (pedon) scale. Improved process-based understanding of underlying processes, continued advances in numerical methods development, and the presence of increasingly powerful computers, are now making it possible to couple the most important flow/transport processes and soil/rock properties relevant to a particular problem. Examples involve multicomponent major ion chemical transport, simulations of the soil-plant-atmosphere continuum, and multiphase flow. Special attention is focused on the problem of preferential flow in variably-saturated structured (fractured or macroporous) media, and the need for more user-friendly software to enable a more effective application of models to a variety of flow/transport problems in research and management. Also discussed is a recently developed hierarchical neural-network approach for improved estimation of the unsaturated soil hydraulic properties, and their uncertainty, from more readily available or more easily measured data.

In: A. Gardenas (ed.), Workshop Proc. “Scale and Variability Issues in the Soil-Hydrological System”, p. 10. Swedish University of Agricultural Sciences, Uppsala, Sweden, Aug. 25-27, 1999.

CHARACTERIZATION AND MEASUREMENT OF THE HYDRAULIC PROPERTIES OF UNSATURATED POROUS MEDIA

M. Th. van Genuchten, F.J. Leij and L. Wu

These Proceedings document 143 edited papers presented at the International Workshop "Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media," held in Riverside, California, October 22-24, 1997. The workshop was organized to review various aspects of water flow and solute transport in unsaturated porous media, particularly with respect to the characterization and measurement of the unsaturated hydraulic properties (water retention, hydraulic conductivity). Knowledge of the hydraulic properties is indispensable for addressing many soil, hydrological, environmental, ecological and agricultural problems.

They are needed in nearly all basic and applied aspects of soil, water, nutrient, and salinity management research (including precision agriculture), and serve as integrated indices for soil quality. They are also needed in models for heat and mass transport near the soil surface to simulate the extent and effects of regional and global climate change, and to interpret or improve the utility of remotely sensed soil moisture data at a variety of spatial scales.

About 220 scientists and engineers from some 20 countries participated in the Workshop; they included soil physicists, hydrologists, chemical and petroleum engineers, geologists, and agricultural engineers. Topics presented at the Workshop ranged from theoretical to application-oriented research, and from modeling to laboratory and field experimentation. The multidisciplinary nature of the Workshop provided unique opportunities for participants to interact with each other, to appreciate issues and opportunities in porous media modeling and characterization, and to discover commonalities and differences between the various disciplines.

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media, Parts* 1 *and* 2, University of California, Riverside, CA, 1602 p., 1999.

MODELING FLOW AND TRANSPORT PROCESSES AT THE LOCAL SCALE

M. Th. van Genuchten, M.G. Schaap, B.P. Mohanty, J. Šimůnek and F.J. Leij

Much progress has been made during the past several decades in attempts to more realistically simulate variably-saturated water flow and solute transport in the subsurface. A large number of conceptual models are now available to predict flow and transport in the vadose zone. In this paper we highlight recent advances in modeling at especially the local scale. Improved understanding of underlying processes, continued advances in numerical methods, and the introduction of increasingly powerful computers now permit comprehensive simulations of the most important physical, chemical and biological processes operative in the unsaturated zone.

Examples include models for mass/energy transport in the soil-plant atmosphere continuum, multicomponent major ion chemistry, and multifluid flow. While the problem of preferential flow remains a challenge, several useful approaches have recently become available to study and model preferential flow in structured media. Increasingly accurate indirect methods, including pedotransfer functions, are now also available for estimating the unsaturated soil hydraulic properties from more readily available or easily measured data. A need still exists for more user-friendly software to enable more effective application of models to a variety of flow and transport problems in research and management.

In: J. Feyen and K. Wiyo (eds.), *Modelling of Transport Process in Soils at Various Scales in Time and Space*, pp. 23-45, Wageningen Pers, Wageningen, The Netherlands, 1999.

RECENT ADVANCES IN VADOSE ZONE FLOW AND TRANSPORT MODELING

M. Th. van Genuchten and E.A. Sudicky

The fate and transport of a variety of chemicals migrating from industrial and municipal waste disposal sites, or applied to. agricultural lands, is increasingly becoming a concern. Once released into the subsurface, these chemicals are subject to a large number of simultaneous physical, chemical, and biological processes, including sorption-desorption, volatilization, and degradation. Depending upon the type of organic chemical involved, transport may also be subject to multiphase flow that involves partitioning of the chemical between different fluid phases. Many models of varying degree of complexity and dimensionality have been developed during the past several decades to quantify the basic physicochemical processes affecting transport in the unsaturated zone. Models for variably saturated water flow, solute transport, aqueous chemistry, and cation exchange were initially developed mostly independently of each other, and only recently has there been a significant effort to couple the different processes involved. Also, most solute transport models in the past considered only one solute. For example, the processes of adsorption-desorption and cation exchange were often accounted for by using relatively simple linear or nonlinear Freundlich isotherms such that all reactions between the solid and liquid phases were forced to be lumped into a single distribution coefficient, and possibly a nonlinear exponent. Other processes such as precipitation-dissolution', biodegradation, volatilization, or radioactive decay were generally simulated by means of simple first- and/or zero-order rate processes. These simplifying approaches were needed to keep the mathematics relatively simple in view of the limitations of previously available computers. The problem of coupling models for water flow and solute transport with multicomponent chemical equilibrium and nonequilibrium models is now increasingly being addressed, facilitated by the introduction of more powerful computers, development of more advanced numerical techniques, and improved understanding of the underlying transport processes.

In this chapter we focus on alternative conceptual approaches for deterministic modeling of solute transport in variably saturated media. Among the topics discussed are single-ion equilibrium and nonequilibrium transport, sorption, degradation, volatilization, and multicomponent transport. Transport in 'Variably saturated structured systems is treated in somewhat more detail to illustrate the potential value of numerical models as useful tools for improving our understanding of the underlying transport processes at the field scale. We also briefly review recent developments in numerical techniques used for solving the governing flow and transport equations, including methods for solving large sparse matrices resulting from spatial and temporal numerical discretization .

In: M. B. Parlange and J. W. Hopmans (eds.). *Vadose Zone Hydrology., Cutting Across Disciplines*, pp. 155-193, Oxford University Press, New York, 1999.

SUFI: AN INVERSE PROGRAM FOR CONDITIONAL PARAMETER ESTIMATION

K.C. Abbaspour, R. Schulin and M. Th. van Genuchten

SUFI (Sequential Uncertainty domain parameter Fitting) is a program that can be used for parameter fitting and parameter conditioning. Parameter fitting refers to a generic fitting objective where a certain function of unknown parameters is fitted to a set of measured data. Parameter conditioning refers to an objective where uncertain model input parameters are conditioned on measured model outputs. Contrary to fitting, in conditioning all measurements are respected by the probabilistic model of input parameters. In this paper the program SUFI is described and two examples are given to demonstrate the conditioning feature of SUFI. In the first example, simultaneous measurements of pressure head and water content are used to condition residual water content, saturated water content, and van Genuchten shape parameters α and n. In the second example measured discharge is used to condition five parameters: residual water content, saturated water content, saturated hydraulic conductivity, and α and n.

In: M. Th. van Genuchten, F. J. Leij and L.Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media*, Part 1, pp. 705-712, University of California, Riverside, CA, 1999.

SIGNIFICANCE OF MACROPOROSITY AND HYDROLOGY FOR SOIL MANAGEMENT AND SUSTAINABILITY OF AGRICULTURAL PRODUCTION IN A HUMID-TROPICAL ENVIRONMENT

L.M. Arya, T.S. Dierolf, A. Sofyan, P. Widjaja-Adhi and M. Th. van Genuchten

This paper analyzes soil-related agronomic constraints in the Sitiung region of Indonesia that are directly related to low nutrient-holding capacity, macroporosity, and rainfall regime. This region receives 2500 to 3000 mm of rainfall per year, but nearly 50% of the rainfall is disposed of rapidly via internal drainage. Although rapid internal drainage reduces the risks of erosion, it leads to infertility, acidity, and Al toxicity. The physical structure of the soils is characterized by stable aggregates, with numerous macropores in the surface and a predominantly microporous subsoil matrix interspersed with a few larger macropores. Macropores account for about 29% of porosity in the surface and between 3 and 6% in the subsoil. The saturated hydraulic conductivity of the matrix containing macropores averages about 300 to 400 cm/day, whereas that of the microporous matrix is generally <1 cm/day. The structure facilitates rapid infiltration and leaching of rainfall. However, little opportunity exists for nutrients moving downward with drainage water to accumulate in the subsoil. The main reason for this seems to be the low hydraulic conductivity and the preponderance of excessive wetness in the subsoil. Drying seems to be essential for movement of nutrients into the subsoil matrix. However, most of the agronomic crops are sensitive to Al toxicity and fail to grow roots deeper than 10 to 15 cm. Thus, they suffer from water stress, despite heavy and frequent rainfall, and fail to cause drying of the subsoil. Problems of acidity Al toxicity, and infertility worsen progressively where agricultural production consists mainly of Al-sensitive crops. Although liming with calcium carbonate improves the soil chemical environment, downward movement of lime is very slow. Deep liming is effective in improving rooting depth, crop water availability, and drying of the subsoil, but the technology is cost- and labor-intensive. Native vegetation, on the other hand, is able to grow roots to considerable depths and causes significant drying of the subsoil, even without soil amendments. Thus, production systems in which locally adapted vegetation of economic value is the main focus seem to be more sustainable and conducive to improving soil conditions.

Soil Science 164(8):586-601, 1999.

MODELING NONWETTING PHASE PERMEABILITY USING ANALYTICAL AND NETWORK MODELS

U. Fischer, M.A. Celia, H. Fluhler and M. Th. van Genuchten

Nonwetting-phase relative permeabilities may be predicted from retention-curve data using a variety of analytical models as well as pore-scale network models. Analytical models that do not account for a discontinuous nonwetting phase fail to predict relative gas permeabilities, while models that account for this phenomenon result in very good predictions. Prediction of relative permeabilities with these analytical models requires stipulation of at least one additional parameter after fitting the retention curve. And these analytical models cannot predict absolute permeabilities without some permeability data. Comparisons of predicted gas permeabilities to measured data for two sandy soils indicate that the network model used provides good estimates of both relative and absolute permeabilities, and can accommodate a discontinuous gas phase, without any parameters beyond those needed to fit the retention curve. While the predicted magnitude of the hysteresis effect in the relative gas permeability functions was not large enough, the predictions obtained with the network model were much better than those calculated with the only analytical model that can be used for prediction of relative permeabilities on the basis of retention data only.

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media*, *Part* 1, pp. 145-154, University of California, Riverside, CA, 1999.

GENERAL MODEL OF THE HYDRAULIC CONDUCTIVITY OF UNSATURATED SOILS

H. Hoffmann-Riem, M. Th. van Genuchten and H. Fluhler

A number of simple theoretical models are widely used to predict the unsaturated hydraulic conductivity of a soil. These models are based on the Hagen-Poiseuille equation, the Young-Laplace equation and several simplifying assumptions regarding the properties of the pore space. We propose a general model which is based on these assumptions but offers greater flexibility than the existing models. The models of Burdine, Mualem and others correspond to particular cases of this general model. A 'soil hydraulic index' is defined to compare the different models.

We then evaluate the validity of some common assumptions by applying different models to data sets taken from the UNSODA data base. To obtain a good fit, at least two parameters of the general model need to be optimized for each data set. In many cases, a reasonable fit requires parameter values that are not physically meaningful. We therefore believe that neither the general model nor the simpler models of Burdine and Mualem should be interpreted as physically-based models.

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media*, *Part* 1, pp. 31-42, University of California, Riverside, CA, 1999.

DISTRIBUTION OF ECOLOGICALLY SIGNIFICANT FRACTIONS OF SELECTED HEAVY METALS IN THE SOIL PROFILE

T. Nemeth, K. Bujtas, J. Csillag, G. Partay, A. Lukacs and M. Th. van Genuchten

The amount of wastes, wastewaters, and sewage sludges produced by agricultural, industrial, and municipal activities is rapidly increasing worldwide. In developing regions of the world this may be simply the result of an improving supply of clean tap water and canalization. Because of increasing environmental awareness, dumping of sewage into surface waters is subject to more strict regulations; thus, the amount of wastewaters subjected to treatments is also increasing in non-industrialized countries. Consequently, much growth in sewage sludge production may be expected, especially when taking into account the higher requirements and standards for wastewater treatment.

In Hungary approximately 1000 million cubic meters (m^3) of wastewater were produced per year in the mid '80s, of which only 187 million m^3 were sufficiently treated, the majority only partially treated, and 173 million m^3 not treated at all. At that time, there was an increasing gap between the development of municipal water supply and of sewage systems, with the latter lagging behind the substantial improvements in water supply. The collection and proper treatment of liquid wastes is still a problem for many smaller municipalities. According to recent data, the amount of sewage in Hungary is above 1 million m^3 per year. About 40% of these sludges are being deposited on agricultural fields and on forest plantations.

One reasonable and economic way to dispose of wastewaters and sludges is to apply them to agricultural fields, thereby exploiting their water and nutrient content. Currently, this practice is becoming increasingly important in many countries. In the early nineties about 30-50% of the sewage sludges were disposed by land application in the majority of the industrialized European countries, which compares to 33% of the annual sludge production in the United States.

In: H. M. Selim. and I. K. Iskandar (eds.). *Fate and Transport of Heavy Metals in the Vadose Zone*, pp. 251-271, Lewis Publ., Boca Raton, FL, 1999.

TWO-MODEL SOIL WATER RETENTION AND FLOW MODEL NUMERICAL SIMULATION

H.A. Sobczuk and M. Th. van Genuchten

Local heterogeneity forces water to flow along complicated paths. Some of the flow paths are interconnected and allow water to flow through the soil system, but some of them are dead ended. The water in dead-end paths will flow until equilibrium of the potential between internal volume and the inlet of the flow path is reached. Any change in the water potential in the inlet will cause a change in the water amount within the volume of dead-end flow. We propose to distinguish two domains within the soil. One, called the mobile domain, takes part in the macroscopic water flow due to a global potential gradient (interconnected paths), and a second, the stagnant domain (containing dead- end pores) where water redistributes according to a local potential gradient.

The proposed model introduces a domain distinction in terms of flow ability. The distinction between both domains is connected with the water flow geometry rather then with the soil phase geometry itself, i.e., it is dependent on the flow intensity and /or direction. Results of numerical simulations in comparison to the Richards equation are presented.

Geophysical Research Abstracts, European Geophysical Society 1(2):328, 1999.

THE IMPORTANCE OF JOHN R. PHILIP'S WORK TO MOTIVATING NUMERICAL ANALYSES OF VARIABLY-SATURATED FLOW

M. Th. van Genuchten and J. Šimůnek

John R. Philip's formidable contributions to understanding and quantifying unsaturated flow and solute transport are too numerous to list. In our research they included his two- and multiple-term infiltration equations, his analytical solutions for horizontal and vertical unsaturated flow, studies of solute transport in aggregated media containing dead-end pores, heat transport in soils, and detailed analytical distributions of water flow around subsurface cavities. We show how several of his studies improved our own research during the past 25 years, especially the testing of numerical solutions of the Richards equation. While variably-saturated flow studies using increasingly sophisticated numerical techniques and more powerful computers have expanded well beyond the analytical applications of Philip's work, sometimes against his wish, they would have been impossible without his leadership and motivation. John Philip will long be remembered in the soil physics and vadose zone hydrology communities.

EOS Transactions Am. Geophys. Union 80(46):498, 2000.

MEASUREMENT AND CHARACTERIZATION OF NONEQUILIBRIUM FLOW IN VARIABLY-SATURATED SOILS

M. Th. van Genuchten, J. Šimůnek and O. Wendroth

Soil hydraulic properties are often measured in the laboratory using a variety of steady-state and transient drying methods (including evaporation and one- or multistep outflow methods). Before such experiments are initiated, samples are usually saturated with the goal of achieving full water saturation. Parameters obtained from such measurements are then often used in simulation models to predict water flow in the near-surface environment. Unfortunately, very little attention is being paid to the fact that saturation levels measured in the laboratory are hardly ever achieved in the field, and that preferential flow typical of field wetting processes are seldom observed using experiments involving a drying process. In this paper we present evidence of nonequilibrium water flow during an upward laboratory infiltration experiment using an undisturbed structured (macroporous) 10-cm long soil sample. Each infiltration was followed by an evaporation experiment to re-establish initial conditions, and to obtain the drying curves. Measured infiltration rated and observed pressure heads within the sample reflect significant nonequilibrium flow associated with air entrapment within the aggregates (the soil matrix) and the presence of a complex flow pattern between the larger inter-aggregate pores and smaller intra-aggregate pores within the soil matrix. The nonequilibrium flow behavior could be well characterized using a two-region dual-permeability model. Implications of the observed data and invoked models are discussed relative to obtaining improved variably-saturated flow predictions in the field.

Int. Workshop and Tutorial Lectures on "Subsurface Flow and Transport Phenomena", Section for Hydrology and Ecology, Faculty of Civil Engineering & Geosciences, Delft Univ. of Technology, The Netherlands, October 23-27, 2000.

UNSATURATED HYDRAULIC PROPERTY ESTIMATION IN SUPPORT OF SUBSURFACE FLOW AND TRANSPORT MODELING

M. Th. van Genuchten

The unsaturated soil hydraulic functions (the water retention and hydraulic conductivity curves) are critical parameters in many hydrologic, subsurface pollution and crop production studies. Current methods to directly measure these highly nonlinear properties are time-consuming and costly, and generally yield only approximate answers in view of the overwhelming heterogeneity of the subsurface. In this presentation we review several methods, including especially pedotransfer functions, for estimating the hydraulic properties from more easily measured data (notably soil texture and bulk density). A hierarchical neural network/bootstrap approach is used to obtain pedotransfer functions estimates of the unsaturated hydraulic functions, and their uncertainty, as a function of increased data availability. The often ignored effects of soil structure and macroporosity on the hydraulic properties, and indirectly on water flow and solute transport predictions, are also discussed. Dual-porosity type functions for the unsaturated hydraulic conductivity of structured media are shown to provide reasonable descriptions of preferential flow in several field experiments. Assuming the presence of immobile water further improved the transport predictions. The use of dual-porosity type hydraulic properties seems justified in view of many data sets which show that the measured saturated hydraulic conductivity is generally about an order of magnitude larger than the saturation end-point of the measured unsaturated hydraulic conductivity curve.

Fourth Int. Conf. on Environmetrics and Chemometrics, Las Vegas, NV, Sept. 18-20, 2000.

EFFECT OF THE SHAPE OF THE SOIL HYDRAULIC FUNCTIONS NEAR SATURATION ON VARIABLY-SATURATED FLOW PREDICTIONS

T. Vogel, M. Th. van Genuchten and M. Cislerova

Relatively small changes in the shape of the soil water retention curve near saturation can significantly affect the results of numerical simulations of variably saturated flow, including the performance of the numerical scheme itself in terms of stability and rate of convergence. In this paper, we use a modified form of the van Genuchten-Mualem (VGM) soil hydraulic functions to account for a very small, but non-zero minimum capillary height, h_s in the soil water retention curve. The modified VGM model is contrasted with the original formulation by comparing simulation results for infiltration in homogeneous soils assuming both constant pressure and constant flux boundary conditions. The two models gave significantly different results for infiltration in fine-textured soils, even for h_s-values as small as -1 cm. Incorporating a small minimum capillary height in the hydraulic properties leads to less non-linearity in the hydraulic conductivity function near saturation and, because of this, to more stable numerical solutions of the flow equation. This study indicates an urgent need for experimental studies that assess the precise shape of the hydraulic conductivity curve near saturation, especially for relatively fine-textured soils. For one example we found considerable improvement in the predicted conductivity function when a value of -2 cm for h_s was used in the modified VGM model.

Adv. Water Resour. 24(2):133-144, 2000.

DYNAMICS OF WATER AND SOLUTE MOVEMENT IN AGGREGATED SOILS

M. Th. van Genuchten, B. Mohanty and J. Šimůnek

Water flow and solute transport are generally considered equilibrium processes which assume that all parts of the liquid phase contribute equally to the flow or transport process. In reality, most field soils exhibit a variety of heterogeneities that cause deviations from equilibrium. Heterogeneity at relatively small scales is reflected by preferential flow through soil macropores and rock fractures. This paper reviews several approaches for modeling flow and transport in structured soils or unsaturated fractured rock. The approaches involve dual- porosity models that assume the presence of distinct mobile and immobile liquid phases in the flow domain, and dual-permeability models that assume that water can flow through both the fractures and soil matrix. Of particular importance in these models are the exchange terms governing water and chemical transfer between the macropores and micropores. Several applications of the two modeling approaches are discussed.

Agronomy Abstract p. 198-199, 1999.

ATMOSPHERIC VOLATILIZATION OF METHYL BROMIDE, 1,3-DICHLOROPROPENE, AND PROPARGYL BROMIDE THROUGH TWO PLASTIC FILMS: TRANSFER COEFFICIENT AND TEMPERATURE EFFECT

D. Wang, S.R. Yates, J. Gan and J.A. Knuteson

Atmospheric emission of methyl bromide (MeBr) and its potential alternative chemicals such as 1,3-dichloropropene (1,3-D) and propargyl bromide (PrBr) can contribute to air pollution and ozone depletion (for MeBr). One of the main sources of these chemicals is from agricultural soil fumigation. To understand the volatilization dynamics, emission of MeBr, 1,3-D, and PrBr through a polyethylene-based high-barrier film (HBF) and a virtually impermeable film (VIF) was measured using an air flow and sampling system that produced >90% mass balance. The experiment was conducted outdoors and was subjected to ambient daily temperature variations. The HBF film was found to be very permeable to 1,3-D and PrBr, but somewhat less permeable to MeBr. The VIF film was very impermeable to 1,3-D, PrBr, or MeBr. Measured volatilization flux, in general, exhibited strong diurnal variations which were controlled by film temperature. Unlike the HBF film, a time lag (~ 12 h) was observed between high-temperatures and high-emission flux values for the VIF film. An impermeable film may be used as an effective means of controlling the atmospheric emission of MeBr and its alternative chemicals.

Atmospheric Environment 33:401-407, 1999.

SPATIAL AND TEMPORAL DISTRIBUTIONS OF 1,3-DICHLOROPROPENE IN SOIL UNDER DRIP AND SHANK APPLICATION AND IMPLICATIONS FOR PEST CONTROL EFFICACY USING CONCENTRATION-TIME INDEX

D. Wang and S.R. Yates

A field experiment was conducted to study the spatial and temporal distributions of (EZ)1,3-dichloropropene (1,3-D) in the soil and effects on pest control efficacy. An emulsifiable concentrate formulation of 1,3-D (Telone EC) was applied with drip irrigation at 47kg AI ha^{-1} to two different depths (2.5 and 20.3 cm, respectively). Comparisons were made between the two drip treatments and a direct shank injection of 1,3-D (Telone II) at 112kg AI ha^{-1}. Concentrations of 1,3-D in soil air were measured at several locations over time to determine the spatial and temporal characteristics, and. to calculate the concentration-time index (CT). Citrus nematodes *(Tylenchulus semipenetrans)* were placed in the fumigated soil at 25 cm depth and their mortality rates were compared to the calculated CT. Distributions of 1,3-D were found to be relatively uniform in both the drip irrigation and the shank injection treatment. An application rate of 47kg ha^{-1} with drip irrigation was sufficient to achieve significant concentration levels in soil beds. Applying 1,3-D with direct shank injection at 112 kg ha^{-1} extended the measurable concentration levels to the furrows between the soil beds and to a depth of 1 m below the soil surface. Effective control of T. *semipenetrans* was achieved with both the drip irrigation and the shank injection. A threshold soil 1,3-D CT value of 12 μg h cm^{-3} was needed to reach a 100% efficacy for T. *semipenetrans.* The study indicates that 1,3-D fumigation may be carried out with drip irrigation at very low rate, and a CT index may be derived to aid in the determination of a minimum effective dosage.

Pesticide Science 55:154-160, 1999.

AUTOMATED SEQUENTIAL SAMPLER FOR COLLECTION OF HIGHLY VOLATILE ATMOSPHERIC CONTAMINANTS

D. Wang, F.F. Ernst and S.R. Yates

Rapid and accurate measurement of atmospheric concentrations of highly volatile organic compounds is important in obtaining reliable information for the assessment of environmental pollution or the volatilization mechanisms of the chemicals. Nonmechanized sample collection requires intensive labor and effort, and may cause large random or systematic errors. An automated solenoid switching system was developed to assist in obtaining precise environmental concentrations of highly volatile organic compounds. The design, construction, and operation are described in the paper for potential application in similar studies. Using this sampling system, two experiments were conducted to determine atmospheric volatilization flux density of three highly volatile and reactive organic compounds (methyl bromide, 1,3-dichloropropene, and propargyl bromide). The automated solenoid switching system significantly reduced the requirements for labor and time. Results from the two experiments indicate that reliable sample collection was achieved. The automated sampling system was also relatively inexpensive and can be easily modified to accommodate a variety of sources, sampling intervals, and multiple number of solenoid valves.

J. Environ. Qual. 28:345-349, 1999.

ACCURACY OF SOIL HYDRAULIC PROPERTY ESTIMATION USING INFILTROMETERS HAVING DIFFERENT DISK SIZES

D. Wang, S.R. Yates and M. Th. van Genuchten

Soil hydraulic properties, such as the saturated hydraulic conductivity (K_s) and the parameter (α) used in exponential expressions of the hydraulic conductivity function, are imporant in modeling water flow and solute transport in unsaturated soil profiles. Tension infiltrometers have become popular instruments for the determination of soil hydraulic properties under field conditions. However, estimated K_s and α values using other independent field or laboratory measurements are often found to be different from those obtained with the infiltrometer method using approximate steady-state solutions. This is likely caused by the variable sizes of the infiltrometer disk used for the infiltration measurement and/or the limitations of steady-state solutions for small disk dimensions. To determine the effect of disk size on parameter estimation, we measured the infiltration in two soils (Arlington sandy loam and Sparta sand) with tension infiltrometers having several disk diameters (5.5-34.5 cm). For each disk size, the infiltration was repeated at multiple supply potentials, while measurements continued until steady-state, so that replicated parameter estimates were obtained. Results suggest that estimated values of (K_s) and α appeared to vary with the size of the infiltrometer disk used. Variations in estimated (K_s) and α values for different disk sizes, or for different potential increments for the same disk, were greater than the possible overestimation with the steady-state solution, as compared to an improved solution for small disk sizes. Discrepancies between tension infiltrometer and other methods in practice are caused probably more by variability within each method such as soil heterogeneity or simplification of the hydraulic conductivity function to an exponential expression, rather than by inherent limitations of the steady-state solutions.

In: M. Th. van Genuchten, F. J. Leij and L. Wu (eds.), Proc. Int. Workshop, *Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media, Part* 1, pp. 563-570, University of California, Riverside, CA, 1999.

TWO-DIMENSIONAL MODEL SIMULATION OF 1,3-DICHLOROPROPENE VOLATILIZATION AND TRANSPORT IN A FIELD SOIL

D. Wang, J.A. Knuteson and S.R. Yates

A modeling study was conducted to simulate 1,3-dichloropropene (1,3-D) emission and concentration distribution in soil profiles when the chemical was applied with subsurface drip irrigation with reduced rate. The purpose was to evaluate the effect on emission reduction as compared with conventional shank injection application. To compare with field measurements, simulated scenarios included a shallow drip application at 2.5 cm, covered with a polyethylene film; a deep drip application at 20.3 cm with bare soil surface; and a conventional shank injection at 30.5 cm with a regular application rate. A convective and diffusive two-dimensional model was used to simulate the simultaneous transport of 1,3-D in both liquid and gaseous phases. Diurnal variations of soil temperature were predicted to calculate 1,3-D diffusion coefficient and the Henry's constant. Predicted 1,3-D emissions compared well with field measurements for the shallow and deep drip irrigation treatments. The model simulation under-predicted 1,3-D emission in the shank injection plot, where other transport mechanisms such as gas phase convection likely occurred during and immediately after application. Results from the modeling study indicate that computer simulation can be used effectively to study the environmental fate and transport of 1,3-D under conditions where vapor phase diffusion and liquid phase convection are the dominant transport mechanisms. Applying 1,3-D with subsurface drip irrigation appeared to be useful for emission reduction.

J. Environ. Qual. 29:639-644, 2000.

ATMOSPHERIC VOLATILIZATION OF 1,3-DICHLOROPROPENE UNDER DIFFERENT APPLICATION METHODS

D. Wang, S.R Yates, F.F. Ernst and J.A. Knuteson

A field experiment was conducted to study the effectiveness of 1,3-dichloropropene (1,3-D) application using subsurface drip irrigation with reduced dosage in decreasing atmospheric emission from soil fumigation. Comparison was made between a shallow drip application at 2.5 cm covered with a polyethylene film, a deep drip application at 20.3 cm with bare soil surface, and a conventional shank injection at 30.5 cm at a regular application rate. Atmospheric emissions of 1,3-D were continuously measured with seven replicated active chambers from the three treatments. Results indicated that total 1,3-D emission loss was over 90% in the shank injection, and 57% and 66% for the deep and shallow drip plots, respectively. The emission loss was extremely high in the shank injection plot since about 80% was emitted from the bed furrows where the slanted shanks left uncompacted fractures. On a per mass basis, the shank plot had 13.7 g lost per meter of field bed, whereas the deep and shallow drip plots had only 3.3 and 3.8 g of 1,3-D lost per meter length, respectively. This is a significant reduction in terms of total 1,3-D emission into the atmosphere. Applying 1,3-D using subsurface drip irrigation with reduced dosage has a great potential for emission reduction.

Water, Air & Soil Pollution 127(1/4):109-123, 2000.

TRANSFORMATION AND DETOXIFICATION OF HALOGENATED FUMIGANTS BY AMMONIUM THIOSULFATE

D. Wang, J. Gan, S.K. Papiernik and S.R. Yates

Fumigants are commonly used at high rates (100-400 kg ha^{-1}) in warm regions to control soil-borne pests. Many fumigants, however, tend to move easily from the treated soil into the atmosphere or groundwater, resulting in air or groundwater pollution. We studied the transformation of the fumigants methyl bromide (MeBr), propargyl bromide (PBr), 1,3-dichloropropene (1,3-D), chloropicrin (CP), and methyl iodide (MeI) by fertilizer ammonium thiosulfate (ATS). All fumigants were rapidly dehalogenated by thiosulfate via nucleophilic substitution, and the rate of transformation followed the order MeBr ≈ MeI > PBr > 1,3-D > CP. For all fumigants, the reaction followed second order kinetics with activation energy of ~73 KS mol^{-1}, suggesting a similar rate-limiting step. In soil, amendment of ATS at 1.0 mmol kg^{-1} accelerated fumigant dissipation by 21-63 times for MeBr, MeI, and PBr and by 4.6-5.5 times for 1,3-D and CP. Preliminary toxicity assays using the luminescent bacterium *Vibrio fisheri* showed, that ATS transformation largely eliminated the acute toxicity of fumigants to this organism. These results suggest that thiosulfate transformation of halogenated fumigants is likely a benign chemical approach that may be used for mitigating environmental and health risks in fumigation.

Environ. Sci. Technol. 34:3717-3721, 2000.

TRANSFORMATION AND DETOXIFICATION OF HALOGENATED FUMIGANTS BY AMMONIUM THIOSULFATE

D. Wang, J. Gan, S.K. Papiernik and S.R. Yates

Fumigants are commonly used at high rates (100-400 kg ha^{-1}) in warm regions to control soil-borne pests. Many fumigants, however, tend to move easily from the treated soil into the atmosphere or groundwater, resulting in air or groundwater pollution. We studied the transformation of the fumigants methyl bromide (MeBr), propargyl bromide (PBr), 1,3-dichloropropene (1,3-D), chloropicrin (CP), and methyl iodide (MeI) by fertilizer ammonium thiosulfate (ATS). All fumigants were rapidly dehalogenated by thiosulfate via nucleophilic substitution, and the rate of transformation followed the order MeBr ≈ MeI > PBr > 1,3-D > CP. For all fumigants, the reaction followed second order kinetics with activation energy of ~73 KS mol^{-1}, suggesting a similar rate-limiting step. In soil, amendment of ATS at 1.0 mmol kg^{-1} accelerated fumigant dissipation by 21-63 times for MeBr, MeI, and PBr and by 4.6-5.5 times for 1,3-D and CP. Preliminary toxicity assays using the luminescent bacterium *Vibrio fisheri* showed, that ATS transformation largely eliminated the acute toxicity of fumigants to this organism. These results suggest that thiosulfate transformation of halogenated fumigants is likely a benign chemical approach that may be used for mitigating environmental and health risks in fumigation.

Environ. Sci. Technol. 34:3717-3721, 2000.

METHODS FOR REMOVING AND DECOMPOSING METHYL BROMIDE FROM FUMIGATION GASES.

S.R. Yates and J. Gan

A method for the removal and rapid decomposition of halogenated fumigation agents is described. A fumigation agent, such as methyl bromide, contained in the gas stream exiting a fumigation chamber or structure is captured on activated carbon or other retentive substrate and rapidly decomposed using thiosulfate and water. The method provides an inexpensive, safe, and on-site executable way to remove and detoxify methyl bromide from fumigation discharge gases, thereby reducing or eliminating methyl bromide emissions into the atmosphere.

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MODELING THE FATE AND TRANSPORT OF VOLATILE PESTICIDES

S.R. Yates, D. Wang, S. Papiernik and J. Gan

Volatilization is a major pathway by which pesticide residues disappear from target areas. This process can be the principal factor affecting efficacy and is a source of unwanted chemicals to the atmosphere. Some volatile pesticides are persistent and can be transported over large distances where they may be deposited in water and soil far removed from their sites of application. Volatile pesticides may also cause other unique problems. For example, methyl bromide, a widely-used soil fumigant, has been shown to damage stratospheric ozone and will soon be phased-out. Since pesticides will likely face increased scrutiny in years ahead, there is a great need to understand the mechanisms that control the emission of pesticides into the atmosphere so that volatilization can be minimized. This paper describes how mathematical models can be used to improve our understanding of pesticide fate and transport and to provide new methods to better manage pesticide application.

American Chemical Society Annual Meeting, New Orleans, Aug. 23, 1999.

GEOSTATISTICS AND SPATIAL VARIABILITY OF SOIL PROPERTIES

S.R. Yates and A.W. Warrick

It has long been recognized that natural processes are subject to variability in both spatial and temporal domains. For example, Jury et al. (1987) has summarized a large number of studies of the spatial variability of water and transport parameters. They found that the observed coefficient of variation for the saturated hydraulic conductivity can range 50 to 300%, infiltration rate 25 to 100% and parameters describing unsaturated hydraulic conductivity 20 to 350%. Clearly, to address agricultural problems in the presence of spatial variations of this level require powerful tools.

Geostatistical methods are popular tools that have found many uses in the analysis of agricultural problems. The methods are generally used to determine various spatially related quantities that characterize the variability of one or more parameters in space and or time. Simple, ordinary and universal kriging methods produce linear estimators that are useful for obtaining estimates of a spatially distributed property over a region, especially at locations for which no data are available. Work on new geostatistical. methods continues, for example, fuzzy logic has been incorporated into estimation methods (Odeh et al., 1992a,b), more efficient methods for obtaining the cross-variogram have been developed (Clark et al., 1989) and nonparametric and nonlinear methods have been used as a means for obtaining the conditional probability of undesirable events.

In: Skaggs (ed.), Agricultural Drainage, pp.1235-1258, 1999.

EMISSION OF PESTICIDES INTO THE AIR

F. van den Berg, G.R. Kubiak, W.G. Benjey, M.S. Majewski, S.R. Yates, G.L. Reeves, H.H. Smelt and A.M.A. van der Linden

During and after the application of a pesticide in agriculture, a substantial fraction of the dosage may enter the atmosphere and be transported over varying distances downwind of the target. The rate and extent of the emission during application, predominantly as spray particle drift, depends primarily on the application method (equipment and technique), the formulation and environmental conditions, whereas the emission after application depends primarily on the properties of the pesticide, soils, crops and environmental conditions. The fraction of the dosage that misses the target area may be high in some cases and more experimental data on this loss term are needed for various application types and weather conditions. Such data are necessary to test spray drift models, and for further model development and verification as well. Following application, the emission of soil fumigants and soil incorporated pesticides into the air can be measured and computed with reasonable accuracy, but further model development is needed to improve the reliability of the model predictions. For soil surface applied pesticides reliable measurement methods are available, but there is not yet a reliable model. Further model development is required which must be verified by field experiments. Few data are available on pesticide volatilization from plants and more field experiments are also needed to study the fate processes on the plants. Once this information is available, a model needs to be developed to predict the volatilization of pesticides from plants, which, again, should be verified with field measurements. For regional emission estimates, a link between data on the temporal and spatial pesticide use and a geographical information system for crops and soils with their characteristics is needed.

Water, Air and Soil Pollution 115:195-218, 1999.

REDUCING FUMIGANT EMISSIONS AFTER SOIL APPLICATION

S.R. Yates, J. Gan, S.K. Papiernik, R. Dungan and D. Wang

Volatilization and soil transformation are major pathways by which pesticides dissipate from treated agricultural soil. Volatilization is a primary source of unwanted agricultural chemicals in the atmosphere and can significantly affect fumigant efficacy. Volatile pesticides may cause other unique problems; for example, the soil fumigant methyl bromide has been shown to damage stratospheric ozone and will soon be phased, out. There is also great concern by persons living near treated fields about the health consequences from inhalation of fumigants. Since replacement fumigants will likely face increased scrutiny in years ahead, there is a great need to understand the mechanisms that control their emission into the atmosphere so these losses can be minimized without loss of efficacy. Recent research has shown that combinations of vapor barriers and soil amendments can be effective in reducing emissions. In this paper, some potential approaches for reducing fumigant emissions to the atmosphere are described.

Phytopathology 90:S103. Publication no. P-2000-0077-SSA, 2000.

ANALYTICAL SOLUTIONS FOR THE TRANSPORT OF VOLATILE ORGANIC CHEMICALS IN UNSATURATED LAYERED SYSTEMS

S.R. Yates, S.K. Papiernik, F. Gao and J. Gan

Several analytical solutions were developed that describe the transport of volatile organic chemicals or other gases in layered porous media. Solutions are presented for a one-dimensional system consisting of either two finite soil layers or a finite layer adjacent to an infinite soil layer. The proposed solutions may be useful for studying the movement of volatile chemicals or other gases in layered soils, as well as for gas movement from soils into passive flux chambers, which are commonly used for measuring the surface volatilization rate. The behavior of the solutions is illustrated by several examples showing the soil gas concentration and the flux density as a function of time. At early times it was found that the flux density into a chamber is relatively constant when the mass transfer coefficient *h* is small. However, the concentration at the soil-chamber interface changes rapidly. For large *h,* the flux density at the interface changes rapidly, and the concentration is relatively constant.

Water Resour. Res. 36(8):1993-2000, 2000.

PREDICTING PESTICIDE VOLATILIZATION FROM SOILS

S.R. Yates, S.K. Papiernik, Q.L. Ma and J. Gan

Due to concerns about public health and environmental contamination, there has been great interest in improving our understanding of the processes and mechanisms that affect pesticide emissions from fields. For many situations, predicting pesticide volatilization has been limited to simple situations that often neglect important environmental conditions such as changes in ambient temperature and/or the effect of micrometeorological conditions. Recent research has shown that changes in ambient temperature can strongly affect methyl bromide volatilization under field conditions. Little research has been conducted that couples atmospheric processes to the volatilization of pesticides from soils. A field study was conducted to measure the volatilization of methyl bromide from a 3.5 ha field. Four methods were used to obtain the volatilization rate as a function of time. A one-dimensional numerical model was developed and used to simulate the fate and transport of methyl bromide from the fumigated field. The numerical simulation simultaneously solves water, heat, and solute transport equations including chemical transport in the vapor phase. Three volatilization boundary conditions were used to assess their accuracy in predicting the volatilization rates. The first two boundary conditions follow stagnant boundary layer theory and use no atmospheric information. For these boundary conditions, one assumes isothermal conditions and the other assumes temperature-dependent conditions. The third boundary condition couples soil and atmospheric processes and was found to provide an accurate and credible simulation of the instantaneous volatilization rates compared to a stagnant boundary layer condition. For some information such as cumulative emissions, the simulations for each boundary condition provided similar results. This indicates that simplified methods may be appropriate for obtaining certain information.

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CONTROLLING AGRICULTURAL EMISSIONS OF METHYL BROMIDE

S.R. Yates, D. Wang, S.K. Papiernik and J. Gan

Over the last 40-50 years methyl bromide (CH3Br) has been used throughout the world to sterilize soils in preparation for planting various high-cash-value fruit and vegetable crops. Highly toxic, CH3Br is very effective in controlling a variety of soil-borne pests, such as nematodes, weeds and fungi. CH3Br has been an important component of agricultural systems in the U.S. and its phase-out is expected to cause financial hardship to agricultural producers. Recent economic assessments estimate that more than $1.5 billion in annual lost production would occur in the United States alone.

In most commercial operations, CH3Br is applied from a tractor pulling two or more metal shanks that cut into the soil. CH3Br is injected into the soil at approximately 25 cm depth from nozzles on the backside of each shank. Simultaneously, the tr actor lays down a 3.5 m wide sheet of 0.025 mm thick high-density polyethylene (HDPE) plastic film; burying one side and gluing the other side to the previous plastic sheet. This creates a series of panels down the field and a continuous cover over the field. Large amounts of CH3Br are applied at rates ranging from 200 to 400 kg/ha.

Emission of CH3Br into the atmosphere is affected to a large degree by the properties of the soil, ambient environmental conditions, application methods, and properties of the plastic film used to seal the surface. Recent research has shown that the traditional HDPE film is largely ineffective in containing CH3Br in soil.

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THEORY AND LABORATORY STUDY OF A TALL PASSIVE CHAMBER FOR MEASURING GAS FLUXES AT SOIL SURFACE

F. Gao, S.R. Yates, M.A. Anderson and M.V. Yates

A tall passive chamber with a height significantly greater than its horizontal dimensions is proposed for measuring fluxes of volatile organic compounds (VOCs) at soil surface. The significant feature of this tall chamber is the presence of a vertical concentration gradient of the target gas in the chamber due to gas emission from soil. The emission and transport behavior of the target gas in the soil-chamber system are analyzed using diffusion theory. A mathematical model is developed to estimate the flux from the soil into the tall chamber, providing the target gas establishes a detectable vertical concentration gradient in the chamber. To obtain the data required for calculating flux, only two gas concentrations ($C1$ and $C2$) at two heights (h_1 and h_2) within the chamber need to be measured at the end of a short chamber placement time (Q). To evaluate the applicability of the tall chamber for measuring flux, several laboratory tests have been conducted using methylene chloride and methyl bromide as the target gases. The results indicate that the proposed tall chamber has a promising potential as a laboratory method for measuring fluxes of volatile organic compounds at soil surface.

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DYNAMISM OF NON-EQUILIBRIUM COMPLEX SYSTEMS AS FLUID FLOW IN SOIL

R.E. Ernst, S.E. Allaire-Leung and S.R. Yates

Preferential flow (PF) is ubiquitous in soil and many processes contributing to it have been intensively studied. However because of its complexity and dynamism, PF is difficult to predict in field conditions. This presentation introduces a theory developed for such complex dynamic systems. We compare the characteristics of these systems to those of PF. Using information found in the literature, we show that PF has fractal characteristics, some type of chain reaction occurs during wetting and drying processes, temporal fluctuation of PF may follow a power spectrum type of behavior, and water flow tends toward critical states at different spatial and temporal scales. We explore the potential of this theory to combine all types of PF processes for field prediction.

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2-D MOVEMENT AND VOLATILIZATION OF FUMIGANTS IN SOILS UNDER DIFFERENT MANAGEMENT METHODS.

S.E. Allaire-Leung, S.R. Yates and F.F. Ernst

Propargyl bromide (3BP) is an alternative fumigant under consideration to replace methyl bromide for pest control in agricultural production. There is an urgent need to study potential management methods that can reduce atmospheric emission when 3BP is injected in the soil. A 2-D laboratory soil column connected to an automatic gas sampler system was used to compare the movement of 3BP in soil and its volatilization due to different initial soil water contents and irrigation timings. A bed-furrow system was made. A tarp was installed above the bed only, and furrow irrigation was applied at different times after 3BP injection. Volatilization was not always higher in the furrow as compared to the bed. Volatilization decreased with frequent short irrigations compared to a long single irrigation. Higher initial soil water content decreased volatilization. Significant convective gas flux occurred in the column during irrigation leading to less volatilization than models predict. Different time-concentration index distributions were obtained in the profile under different irrigation management methods.

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